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(FILE 'HOME' ENTERED AT 14:26:35 ON 30 MAR 2001)

FILE 'REGISTRY' ENTERED AT 14:26:48 ON 30 MAR 2001

L1 1 S 7440-02-0
 L2 1 S 7440-16-6
 L3 1 7440-05-3
 L4 1 S 7440-18-8

claimed metal catalysts

FILE 'HCAPLUS' ENTERED AT 14:34:12 ON 30 MAR 2001

L5 35211 S ?UNSATURAT?(5A)?ESTER?
 L6 6402 S ?HYDROGENAT?(5A)?ESTER?
 L7 455 S L5(L)L6
 L8 844882 S CATALY?
 L9 292165 S L1-4
 L10 1741 S L6(L)L8
 L11 151 S L6(L)L9
 L12 145 S L10 AND L11
 L13 6 S L12 AND ?ALLYL? *6 citations*
 L14 110339 S RECYCL?
 L15 1182 S LIQUID(W) PHASE(W) REACTION
 L16 13524 S FIXED(W) BED
 L17 871 S L5(5A)?ALLYL?
 L18 8 S L17 AND L6
 L19 8 S L18 NOT L13
 L20 2 S L19 AND (L9 OR L8) *2 cites*
 L21 6 S L19 NOT L20 *6 cites*
 L22 1 S L7 AND L14
 L23 20 S L7 AND ALLYL?
 L24 224 S L7 AND L8
 L25 47 S L24 AND L9
 L26 3 S L7 AND (L15-16)
 L27 0 S (L26 OR L22) AND L23 AND L25
 L28 0 S (L26 OR L22) AND L23
 L29 4 S (L26 OR L22)
 L30 4 S L29 NOT L18-21
 L31 4 S L30 NOT L13 *4 cites*
 L32 3 S L23 AND L25
 L33 0 S L32 NOT (L13 OR L18-21 OR L31) *no good*
 L34 13 S L23 NOT (L13 OR L18-21 OR L31)
 L35 1 S L17(5A)HYDROGENAT? *1 cite*

text searching

FILE 'CASREACT' ENTERED AT 15:04:12 ON 30 MAR 2001

L36 STR
 L37 4 S L36
 L38 351 S L36 FUL
 L39 331 S L38/COM
 L40 2645 S 7440-02-0/CAT
 L41 551 S 7440-16-6/CAT
 L42 14310 S 7440-05-3/CAT
 L43 237 S 7440-18-8/CAT
 L44 25 S L39(L)L40-43
 L45 11 S L44 AND HYDROGENAT? *all citations*
 L46 STR L36
 L47 17 S L46
 L48 STR L46
 L49 13 S L48
 L50 16887 S L40-43
 L51 0 S L48 SSS SAM SUB=L50
 L52 13 S L48 SSS SAM SUB=L38
 L53 0 S L52 NOT L49
 L54 270 S L48 SSS FUL SUB=L38
 L55 33 S L54 AND L50
 L56 25 S L55 NOT L45
 L57 1 S L56 AND (ALLYL OR VINYL) (5A) ESTER
 L58 6 S L56 AND HYDROGENAT?
 L59 7 S L57-58 *7 citations*

reaction searching

FILE 'REGISTRY' ENTERED AT 15:52:25 ON 30 MAR 2001

L60 STR L48
 L61 SCREEN 1838
 L62 50 S L60 NOT L61
 L63 20 S L62 AND NC=1
 L64 12941 S L60 NOT L61 FUL *12,941 cpds*
 L65 11005 S L64/COM

str searching
and next page

SEARCHED BY SUSAN HANLEY 305-4053

Page 1

no ring in str

REYES 09/582,495

L66 2977 S L65 NOT PMS/CI *no polymers*
L67 2932 S L66 AND NC=1 *only one component (no mixtures)*

FILE 'HCAPLUS' ENTERED AT 16:02:43 ON 30 MAR 2001

L68 17876 S L67 *17,876 cites for L67 cpds*
L69 3766 S L68(L)PREP/RL
L70 115 S L68(L)HYDROGENAT?
L71 34 S L69 AND L70
L72 10 S L71 AND L9
~~L73~~ 9 S L72 NOT (L13 OR L18-21 OR L31) *9 citations*
L74 39 S L70 AND L9
L75 25 S L74 NOT (L72 OR L13 OR L18-21 OR L31)
L76 0 S L75 AND L14-16
~~L77~~ 3 S L6 AND L75 *3 cites*

STR for 1st cas react search

REYES 09/582,495

=> d que 139

L36 STR

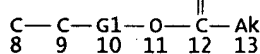
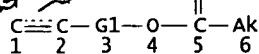
RRT

7

PRO

14

reactant



product

REP G1=(0-1) C

NODE ATTRIBUTES:

CONNECT IS E1 RC AT 6

CONNECT IS E1 RC AT 13

DEFAULT MLEVEL IS ATOM

GGCAT IS LOC AT 6

GGCAT IS LOC AT 13

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 14

STEREO ATTRIBUTES: NONE

*****MAPPINGS*****

NOD	SYM	ROL	NOD	SYM	ROL
1	C	RRT	8	C	PRO
2	C	RRT	9	C	PRO
8	C	PRO	1	C	RRT
9	C	PRO	2	C	RRT

L38 351 SEA FILE=CASREACT SSS FUL L36 (838 REACTIONS)
L39 331 SEA FILE=CASREACT ABB=ON PLU=ON L38/COM

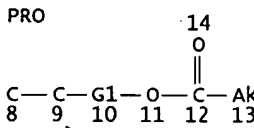
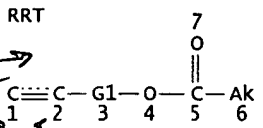
2nd search on CASREACT

REYES 09/582,495

=> d_queue 154

L36 STR

parent STR



product

REP G1=(0-1) C
 NODE ATTRIBUTES:
 CONNECT IS E1 RC AT 6
 CONNECT IS E1 RC AT 13
 DEFAULT MLEVEL IS ATOM
 GGCAT IS LOC AT 6
 GGCAT IS LOC AT 13
 DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
 RING(S) ARE ISOLATED OR EMBEDDED
 NUMBER OF NODES IS 14

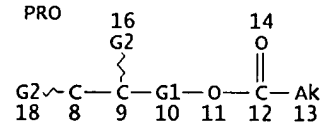
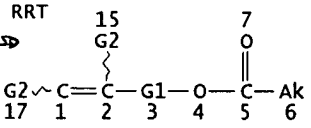
STEREO ATTRIBUTES: NONE

****MAPPINGS****

NOD SYM	ROL	NOD SYM	ROL
1 C	RRT	8 C	PRO
2 C	RRT	9 C	PRO
8 C	PRO	1 C	RRT
9 C	PRO	2 C	RRT

L38 351 SEA FILE=CASREACT SSS FUL L36 (838 REACTIONS)
 L48 STR

subset search - narrowing the search



Ak @19

reactant

open

REP G1=(0-1) C
 VAR G2=H/19
 NODE ATTRIBUTES:
 CONNECT IS E1 RC AT 6
 CONNECT IS E1 RC AT 13
 CONNECT IS E1 RC AT 19
 DEFAULT MLEVEL IS ATOM
 GGCAT IS LOC SAT AT 6
 GGCAT IS LOC SAT AT 13
 DEFAULT ECLEVEL IS LIMITED

G2 is H or AK

product

GRAPH ATTRIBUTES:
 RING(S) ARE ISOLATED OR EMBEDDED
 NUMBER OF NODES IS 19

STEREO ATTRIBUTES: NONE

****MAPPINGS****

NOD SYM	ROL	NOD SYM	ROL
1 C	RRT	8 C	PRO
2 C	RRT	9 C	PRO
8 C	PRO	1 C	RRT
9 C	PRO	2 C	RRT

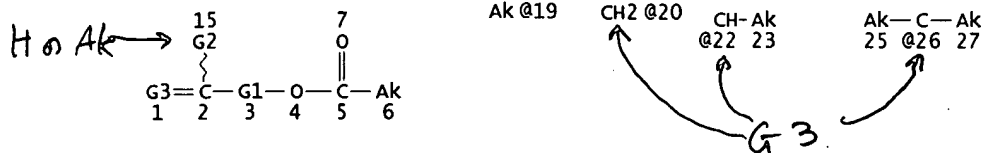
L54 270 SEA FILE=CASREACT SUB=L38 SSS FUL L48 (616 REACTIONS)

STR for HCAPLUS

REYES 09/582,495

=> d que 168)

L60 STR



REP G1=(0-1) C
VAR G2=H/19
VAR G3=20/22/26

NODE ATTRIBUTES:

CONNECT IS E1 RC AT 6
CONNECT IS E1 RC AT 19
CONNECT IS E1 RC AT 23
CONNECT IS E1 RC AT 25
CONNECT IS E1 RC AT 27
DEFAULT MLEVEL IS ATOM
GGCAT IS LOC SAT AT 6
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 15

STEREO ATTRIBUTES: NONE

L61 SCR 1838
L64 12941 SEA FILE=REGISTRY SSS FUL L60 NOT L61
L65 11005 SEA FILE=REGISTRY ABB=ON PLU=ON L64/COM
L66 2977 SEA FILE=REGISTRY ABB=ON PLU=ON L65 NOT PMS/CI
L67 2932 SEA FILE=REGISTRY ABB=ON PLU=ON L66 AND NC=1
L68 17876 SEA FILE=HCAPLUS ABB=ON PLU=ON L67

=> d bib abs hitstr 177 1

L77 ANSWER 1 OF 3 HCAPLUS COPYRIGHT 2001 ACS

AN 1996:398840 HCAPLUS

DN 125:68747

TI Preparation of zirconium phosphate-phosphonate containing complexing groups

AU Fu, Xiangkai; He, Youqiu; Ma, Xuebing; Liu, Changhua; Wen, Shuying

CS Coll. Chem. Chem. Eng., Southwest China Normal Univ., Chungking, 630715, Peop. Rep. China

SO Cuihua Xuebao (1996), 17(3), 260-262

CODEN: THHPD3; ISSN: 0253-9837

DT Journal

LA Chinese

AB A new type of supports for supported complex catalysts, zirconium phosphate-phosphonate bearing complexing group $Zr(HPO_4)_2 \cdot x(O_3PG)x \cdot cntdot.H_2O$ or $Zr(HPO_3)_2 \cdot x-(O_3PG)x \cdot cntdot.H_2O$ ($G = CH_2NET_2$, CH_2NBU_2 , $CH_2NCH_2CO_2H$, $CH_2N(CH_2CO_2H)_2 \cdot cntdot.CH_2NCH_2-CH_2OH$, $CH_2N(CH_2CH_2OH)_2$, etc.), was prepd. for the first time. The yield, IR spectra, compn. and complexing ability of the supports were discussed. The supported palladium catalysts prepd. from these supports by complexing $PdCl_2$ exhibit very high activity for hydrogenation of substituted olefins under atm. pressure, and can be reused for many times without serious loss in activity.

IT 108-05-4, Acetic acid ethenyl ester, reactions

RL: RCT (Reactant)

(hydrogenation of; prepn. of zirconium phosphate-phosphonate contg. complexing groups for catalysts)

RN 108-05-4 HCAPLUS

CN Acetic acid ethenyl ester (9CI) (CA INDEX NAME)

ACO-CH=CH₂

IT 7440-05-3, Palladium, uses

RL: CAT (Catalyst use); USES (Uses)

(prepn. of zirconium phosphate-phosphonate contg. complexing groups for catalysts)

RN 7440-05-3 HCAPLUS

CN Palladium (8CI, 9CI) (CA INDEX NAME)

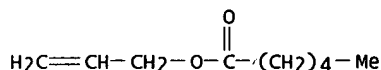
Pd

=> d bib abs hitstr 177 2

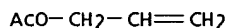
L77 ANSWER 2 OF 3 HCAPLUS COPYRIGHT 2001 ACS
 AN 1991:448638 HCAPLUS
 DN 115:48638
 TI Hydrogenation of allyl esters of saturated carboxylic acids in the presence of a nickel-titanium-aluminum catalyst
 AU Il'khamdzhanov, P.; Mirkomilov, T. M.; Makhsnnov, A. G.; Makhmudova, Z.
 CS Tashk. Politekh. Inst., Tashkent, USSR
 SO Uzb. Khim. Zh. (1991), (2), 45-7
 CODEN: UZKZAC; ISSN: 0042-1707
 DT Journal
 LA Russian
 AB Factors contributing to the optimization of hydrogenation of short-chain and fatty acid allyl esters in the presence of a Ni-Ti-Al catalyst were discussed. Among alc. solvents, the hydrogenation rate of caprylic acid was highest for MeOH and EtOH; the hydrogenation rate for fatty acid esters was max. in hexane and ligroine. The rate of hydrogenation increased with the rate of mixing in the range 100-400 shakes/min, and remained const. at higher shaking rates.
 IT 7440-02-0, Nickel, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts contg., for hydrogenation of carboxylic and fatty acid allyl esters)
 RN 7440-02-0 HCAPLUS
 CN Nickel (8CI, 9CI) (CA INDEX NAME)

Ni

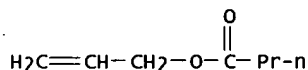
IT 123-68-2, Allyl hexanoate 591-87-7, Allyl acetate
 2051-78-7
 RL: RCT (Reactant)
 (hydrogenation of, in presence of nickel-titanium-aluminum catalyst, optimization of)
 RN 123-68-2 HCAPLUS
 CN Hexanoic acid, 2-propenyl ester (9CI) (CA INDEX NAME)



RN 591-87-7 HCAPLUS
 CN Acetic acid, 2-propenyl ester (9CI) (CA INDEX NAME)



RN 2051-78-7 HCAPLUS
 CN Butanoic acid, 2-propenyl ester (9CI) (CA INDEX NAME)



=> d bib abs hitstr 177 3

L77 ANSWER 3 OF 3 HCAPLUS COPYRIGHT 2001 ACS
 AN 1988:132932 HCAPLUS
 DN 108:132932
 TI Study of poly(vinyl-p-dimethylaminobenzal)-metal complexes for catalytic hydrogenation
 AU Jiang, Cuanyu; Zhang, Xiankang; Du, Jianpin; Hua, Jiadong; Fang, Shibi; Jiang, Yingyan
 CS Shanghai Univ. Sci. Technol., Shanghai, Peop. Rep. China
 SO Shanghai Keji Daxue Xuebao (1987), (1), 81-74
 CODEN: SKDXDH
 DT Journal
 LA English
 AB Supported vinyl acetal polymers were prep'd. from poly(vinyl alc.), SiO₂, and p-Me₂NC₆H₄CHO and crosslinked with glutaraldehyde. Pt and Pd complexes of the crosslinked polymers were used to hydrogenate acrylic acid, methacrylic acid, acrylonitrile, vinylpropanol, Bu acrylate, Me acrylate, Me methacrylate, vinyl acetate, PhNO₂, styrene, and cyclohexene. Acrylic acid and Bu acrylate were the most readily hydrogenated, EtOAc solvent had the most beneficial effect on hydrogenation, 46.degree. was the optimum temp. The polymer Pt complex was more effective than H₂PtCl₆.
 IT 7440-05-3D, Palladium, complexes with silica-supported glutaraldehyde-crosslinked vinyl acetal polymers based on dimethylaminobenzaldehyde
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts, for hydrogenation of vinyl and acrylic and unsatd. compds.)
 RN 7440-05-3 HCAPLUS
 CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 108-05-4, reactions
 RL: RCT (Reactant)
 (hydrogenation of, catalysts for, platinum and palladium complexes with dimethylaminobenzaldehyde-based silica-supported vinyl acetal polymers as)
 RN 108-05-4 HCAPLUS
 CN Acetic acid ethenyl ester (9CI) (CA INDEX NAME)

$$\text{ACO}-\text{CH}=\text{CH}_2$$

=> d bib abs hitstr 120 1

(L20 ANSWER 1 OF 2 HCAPLUS) COPYRIGHT 2001 ACS

AN 1997:509106 HCAPLUS

DN 127:190471

TI Preparation of saturated esters from unsaturated esters

IN Tanaka, Yasutaka; Fukuya, Kazuaki

PA Daicel Chemical Industries, Ltd., Japan.

SO Jpn. Kokai Tokkyo Koho, 4 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 09194427	A2	19970729	JP 1996-24686	19960118

OS CASREACT 127:190471; MARPAT 127:190471

AB Satd. esters are prepd. by hydrogenation of
R1R2C:CR3CR4R5O2CR6 (R1-R5 = C1-10 alkyl, H; R6 = C1-10 alkyl) by using
catalysts contg. 10-100 wt.% Ni. Allyl acetate and H were passed
through N111 (Ni catalyst supported on a carrier)-packed column
at 150.degree. over 8 h to give 92.8% Pr acetate.

IT 7440-02-0, Raney nickel, uses

RL: CAT (Catalyst use); USES (Uses)

(N 154; prepn. of satd. esters from unsatd. esters by using Ni
catalysts)

RN 7440-02-0 HCAPLUS

CN Nickel (8CI, 9CI) (CA INDEX NAME)

Ni

=> d bib abs hitstr 120 2

L20 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2001 ACS
 AN 1971:475535 HCAPLUS
 DN 75:75535
 TI Reduction of unsaturated compounds containing oxygen
 AU Russell, Thomas W.; Hoy, Richard C.
 CS Dep. Chem., East. New Mexico Univ., Portales, N. Mex., USA
 SO J. Org. Chem. (1971), 36(14), 2018-19
 CODEN: JOCEAH
 DT Journal
 LA English
 AB The C-C .pi.-bonds of allylic alcs., diols, ethers, and esters, and .alpha.,.beta.-unsatd. acids, esters, ketones and aldehydes are reduced by hydrogenation over Ni boride. 1,2-Epoxyalkanes and cinnamic acid (trans) are unaffected. The epoxyalkanes do not rearrange to carbonyl compds.

=> d ind 2

L20 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2001 ACS
 CC 21 (General Organic Chemistry)
 ST ~~oxygenated unsatd compd redn~~; nickel boride hydrogenation catalyst
 ; allylic compd oxygenated redn
 IT Acids, reactions
 Alcohols, reactions
 Aldehydes, reactions
 Esters, reactions
 Ethers
 Ketones, reactions
 RL: RCT (Reactant)
 (hydrogenation of unsaturated, catalysts for)
 IT Hydrogenation catalysts
 (nickel boride, for unsaturated oxygen compds.)
 IT Nickel boride
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts, for hydrogenation of unsaturated oxygen compds.)
 IT Oxygen, unsaturated
 RL: RCT (Reactant)
 (hydrogenation of, catalysts for)

Reduction

=> d bib abs hitstr 1

L73 ANSWER 1 OF 9 HCAPLUS COPYRIGHT 2001 ACS

AN 1998:498375 HCAPLUS

DN 129:175360

TI Regeneration of palladium catalysts for hydrogenation of diacetoxybutene into diacetoxybutane

IN Murai, Nobuyuki; Iwasaka, Hiroshi; Nishimura, Seijiro

PA Mitsubishi Chemical Industries Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 10202106	A2	19980804	JP 1997-5981	19970117
AB	The title catalysts comprising Pd supported on activated C, are regenerated by treating with steam and/or hot water. A mixt. contg. 84.5 wt.% 1,4-diacetoxybutene (I) and 9.5 wt.% 3,4-diacetoxybutene (II) was hydrogenated over Pd/activated-C by continuously feeding into a reactor at 50 g/h, resulting in residual I and II contents of 0.4 and 0.01 wt.%, resp., 4 h later and 2.5 and 0.2 wt.%, resp., 8000 h later. Then, the catalyst with lowered activity, was regenerated by treating with steam at 100.degree. for 7 h to recover its initial activity.				
IT	7440-05-3, Palladium, uses RL: CAT (Catalyst use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses) (steam or hot water in regeneration of Pd/activated-C catalysts for hydrogenation of diacetoxybutene into diacetoxybutane)				
RN	7440-05-3 HCAPLUS				
CN	Palladium (8CI, 9CI) (CA INDEX NAME)				

Pd

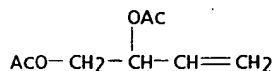
IT 18085-02-4P, 3,4-Diacetoxy-1-butene

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)

(steam or hot water in regeneration of Pd/activated-C catalysts for hydrogenation of diacetoxybutene into diacetoxybutane)

RN 18085-02-4 HCAPLUS

CN 3-Butene-1,2-diol, diacetate (8CI, 9CI) (CA INDEX NAME)

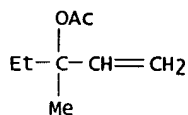


=> d bib abs hitstr 2

L73 ANSWER 2 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1998:375150 HCAPLUS
 DN 129:175335
 TI Simple preparation of bimetallic palladium-copper catalysts for selective
 liquid phase semihydrogenation of functionalized acetylenes and
 propargylic alcohols
 AU Spee, M. P. R.; Grove, D. M.; Van Koten, G.; Geus, J. W.
 CS Debye Institute, Department of Metal-Mediated Synthesis, Utrecht
 University, Utrecht, 3584 CH, Neth.
 SO Stud. Surf. Sci. Catal. (1997), 108(Heterogeneous Catalysis and Fine
 Chemicals IV), 313-319
 CODEN: SSCTDM; ISSN: 0167-2991
 PB Elsevier Science B.V.
 DT Journal
 LA English
 OS CASREACT 129:175335
 AB Silica supported palladium-copper catalysts were obtained in a fast and
 simple prepn. method by redn. of bimetallic organometallic compds. on the
 support surface in the liq. phase at room temp. The supported bimetallic
 particles were analyzed by TEM and EDAX. Directly after prepn. the silica
 supported palladium-copper catalysts could be used in the
 semihydrogenation of triple bonds. The catalysts are selective in the
 hydrogenation of acetylenes and propargylic alcs. giving high yields of
 either olefins or satd. hydrocarbons, depending on reaction time. In
 addn., the catalytic system shows reasonable selectivity towards
 cis-olefins in the hydrogenation of disubstituted acetylenes.
 IT 7440-05-3DP, Palladium, silica-bound
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
 USES (Uses)
 (prepn. of silica-supported bimetallic palladium-copper catalysts for
 the chemo- and stereoselective hydrogenation of alkynes and alkynols)
 RN 7440-05-3 HCAPLUS
 CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 919-35-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of silica-supported bimetallic palladium-copper catalysts for
 the chemo- and stereoselective hydrogenation of alkynes and
 alkynols)
 RN 919-35-7 HCAPLUS
 CN 1-Penten-3-ol, 3-methyl-, acetate (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)



=> d bib abs hitstr 3

L73 ANSWER 3 OF 9 HCAPLUS COPYRIGHT 2001 ACS

AN 1998:208655 HCAPLUS

DN 128:230563

TI Procedure for production of butanediol by the catalytic acetoxylation of butadiene followed by hydrogenation and hydrolysis

IN Murai, Nobuyuki; Iwasaka, Hiroshi

PA Mitsubishi Chemical Corp., Japan

SO Ger. Offen., 8 pp.

CODEN: GWXXBX

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 19741729	A1	19980326	DE 1997-19741729	19970922
	CA 2215544	AA	19980324	CA 1997-2215544	19970915
	JP 10152450	A2	19980609	JP 1997-250287	19970916
PRAI	JP 1996-251455		19960924		

AB Butanediol (i.e., 1,4-butanediol), useful as a monomer and chem. intermediate, is prepd. in high yield and selectivity by the catalytic acetoxylation of butadiene with AcOH in the presence of a Pd catalyst, hydrogenation of the diacetoxybutene intermediate to diacetoxybutane, and hydrolysis of the diacetoxybutane which contains .ltoreq.0.5% diacetoxyoctane. A process flow diagram is presented.

IT 7440-05-3, Palladium, uses

RL: CAT (Catalyst use); USES (Uses)

(procedure for prodn. of 1,4-butanediol by the catalytic acetoxylation of butadiene followed by hydrogenation and hydrolysis)

RN 7440-05-3 HCAPLUS

CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

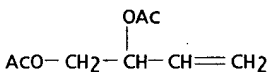
IT 18085-02-4P, Diacetoxybutene

RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)

(procedure for prodn. of 1,4-butanediol by the catalytic acetoxylation of butadiene followed by hydrogenation and hydrolysis)

RN 18085-02-4 HCAPLUS

CN 3-Butene-1,2-diol, diacetate (8CI, 9CI) (CA INDEX NAME)



=> d bib abs hitstr 4

L73 ANSWER 4 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1992:489825 HCAPLUS
 DN 117:89825
 TI Selective hydrogenation of olefins
 IN Chalk, Alan J.; Wertheimer, Laszlo V.
 PA Givaudan Corp., USA
 SO U.S., 10 pp.
 CODEN: USXXAM
 DT Patent
 LA English
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5118837	A	19920602	US 1987-13608	19870212
OS	CASREACT 117:89825; MARPAT 117:89825				
AB	Olefins contg. more than 1 double bond were selectively hydrogenated in the presence of a catalyst system consisting of a heterogeneous Ru catalyst, water, and a modifier. The hydrogenation is carried out at 0-100.degree. and pressures up to 2000 psig. Thus, 8.4 g 1-acetoxyocta-2,7-diene (I) was hydrogenated for 1.5 h in a mixt. of 3 mL H ₂ O, 0.12 g Ru/C, 1.15 mmol P(OBu) ₃ as a modifier and 15 mL EtOH at 25.degree. and 50 psi to give 98.9% conversion of I with 98.4 selectivity for 1-acetoxyoct-2-ene, which was present in 97.3% purity.				
IT	2371-13-3P, 1-Acetoxyoct-2-ene RL: SPN (Synthetic preparation); PREP (Preparation) (prepn. of, by selective hydrogenation of diene)				
RN	2371-13-3 HCAPLUS				
CN	2-Octen-1-ol, acetate (7CI, 8CI, 9CI) (CA INDEX NAME)				

$$\text{ACO}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{Me}$$

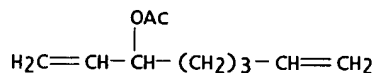
IT 7440-16-6, Rhodium, uses 7440-18-8, Ruthenium, uses
 RL: USES (Uses)
 (selective hydrogenation catalysts, for dienes)
 RN 7440-16-6 HCAPLUS
 CN Rhodium (8CI, 9CI) (CA INDEX NAME)

Rh

RN 7440-18-8 HCAPLUS
 CN Ruthenium (8CI, 9CI) (CA INDEX NAME)

Ru

IT 3491-26-7, 3-Acetoxyocta-1,7-diene 3491-27-8,
 1-Acetoxyocta-2,7-diene
 RL: RCT (Reactant)
 (selective hydrogenation of)
 RN 3491-26-7 HCAPLUS
 CN 1,7-Octadien-3-ol, acetate (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 3491-27-8 HCAPLUS
 CN 2,7-Octadien-1-ol, acetate (7CI, 8CI, 9CI) (CA INDEX NAME)

$$\text{ACO}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2$$

=> d bib abs hitstr 5

L73 ANSWER 5 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1990:138372 HCAPLUS
 DN 112:138372
 TI Giant palladium clusters as catalysts of oxidative reactions of olefins and alcohols
 AU Vargaftik, M. N.; Zagorodnikov, V. P.; Stolyarov, I. P.; Moiseev, I. I.; Kochubey, D. I.; Likholobov, V. A.; Chuvilin, A. L.; Zamaraev, K. I.
 CS N. S. Kurnakov Inst. Gen. Inorg. Chem., Moscow, 117907, USSR
 SO J. Mol. Catal. (1989), 53(3), 315-48
 CODEN: JMCADS; ISSN: 0304-5102
 DT Journal
 LA English
 AB Giant cationic palladium clusters approximated as Pd₅₆L₆₀(OAc)₁₈₀ [L = 1,10-phenanthroline (phen), 2,2'-bipyridine] and Pd₅₆phen₆₀O₆₀(PF₆)₆₀ were synthesized and characterized with high resolu. TEM, SAXS, EXAFS, IR and magnetic susceptibility data. The results of these studies suggest that L and O ligands are bound to Pd atoms located on the surfaces of close-packed metal skeletons of the clusters, while OAc- and PF₆- anions are outer-sphere ligands. Under mild conditions (293-363 K, 1 atm) the giant palladium clusters catalyze oxidative acetoxylation of ethylene into vinyl acetate, propylene into allyl acetate, and toluene into benzyl acetate; oxidn. of primary aliph. alcs. into esters; and conversion of aldehydes into acetals. Kinetics of the oxidative acetoxylation of ethylene and propylene in solns. of the giant clusters were studied. A mechanism for these reactions is proposed, which includes the following steps: coordination of reagents by the cluster, oxidative addn. of alkene to a Pd-Pd fragment and transfer of an electron pair from a Pd-H, Pd-vinyl, or Pd-allyl fragment to a coordinated mol. of oxidant [O₂, peroxide, Pd(II)].
 IT 108-05-4, Acetic acid ethenyl ester, reactions
 RL: RCT: (Reactant)
 (hydrogenation of)
 RN 108-05-4 HCAPLUS
 CN Acetic acid ethenyl ester (9CI) (CA INDEX NAME)

ACO-CH=CH₂

IT 7440-05-3DP, Palladium, phenanthroline and bipyridine cluster complexes
 RL: PREP (Preparation)
 (prepn. of)
 RN 7440-05-3 HCAPLUS
 CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 591-87-7P, Allyl acetate
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of, from acetoxylation of propylene)
 RN 591-87-7 HCAPLUS
 CN Acetic acid, 2-propenyl ester (9CI) (CA INDEX NAME)

ACO-CH₂-CH=CH₂

=> d bib abs hitstr 6

L73 ANSWER 6 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1983:504731 HCAPLUS
 DN 99:104731
 TI Selective hydrogenation of unsaturated oxo compounds
 AU Sagindykova, S. M.; Kartonozhkina, O. I.; Konuspaev, S. R.
 CS USSR
 SO Deposited Doc. (1982), VINITI 3814-Pt.2-82, 66-9 Avail.: VINITI
 DT Report
 LA Russian
 AB The effects of inorg. salt additives on the hydrogenation of citral, 4-Me2CHC6H4CH:CMCHO (I), dehydrolinalool (II), and dehydrolinalool acetate (III) were examd. When citral and I were hydrogenated on Ni/Cr2O3, the selectivity for citronellal and 4-Me2CHC6H4CH2CHMeCHO was increased by several salts, esp. KI with citral and K2CO3 with I. In the hydrogenation of II on Pd/Al2O3, addn. of CdSO4 caused the reaction to stop after absorption of 1 mol H2; in the case of III absorption of 2 mol H2 occurred in the presence of CdSO4.
 IT 7440-02-0, uses and miscellaneous 7440-16-6, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts, for hydrogenation of citral and isopropylmethylcinamaldehyde)
 RN 7440-02-0 HCAPLUS
 CN Nickel (8CI, 9CI) (CA INDEX NAME)

Ni

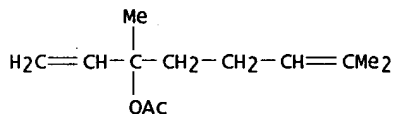
RN 7440-16-6 HCAPLUS
 CN Rhodium (8CI, 9CI) (CA INDEX NAME)

Rh

IT 7440-05-3, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts, for hydrogenation of dihydrolinalool and its acetate)
 RN 7440-05-3 HCAPLUS
 CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 115-95-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of, by hydrogenation of dihydrolinalool, effect of cadmium sulfate on)
 RN 115-95-7 HCAPLUS
 CN 1,6-Octadien-3-ol, 3,7-dimethyl-, acetate (8CI, 9CI) (CA INDEX NAME)

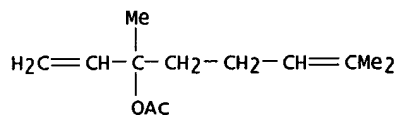


=> d bib abs hitstr 7

L73 ANSWER 7 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1981:533174 HCAPLUS
 DN 95:133174
 TI Catalytic hydrogenation of dehydrolinalool and dehydrolinalyl acetate
 AU Cervený, Libor; Kuncová, Marcela; Ruzicka, Vlastimil
 CS Dep. Org. Technol., Prague Inst. Chem. Technol., Prague, 166 28, Czech.
 SO Collect. Czech. Chem. Commun. (1981), 46(5), 1258-61
 CODEN: CCCCAK; ISSN: 0366-547X
 DT Journal
 LA English
 AB Hydrogenation of dehydrolinalool and dehydrolinalyl acetate in the liq.
 phase over Pd on CaCl₂ (partially deactivated by Pd) at 20.degree. under
 atm. pressure gave linalool and linalyl acetate with 99-99.5 and 95-6%,
 resp., selectivities.
 IT 7440-05-3, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalyst, for hydrogenation of dehydrolinalool and dehydrolinalyl
 acetate)
 RN 7440-05-3 HCAPLUS
 CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 115-95-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of, by hydrogenation of dehydrolinalyl acetate)
 RN 115-95-7 HCAPLUS
 CN 1,6-Octadien-3-ol, 3,7-dimethyl-, acetate (8CI, 9CI) (CA INDEX NAME)

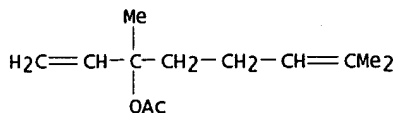


=> d bib abs hitstr 8

L73 ANSWER 8 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1981:46730 HCAPLUS
 DN 94:46730
 TI Hydrogenation of dehydrolinalyl acetate into linalool acetate on supported palladium catalysts
 AU Pak, A. M.; Sokol'skii, D. V.; Tsai, E. M.; Pogorel'skii, A. P.; Bakhtinov, A. A.
 CS Inst. Org. Katal. Elektrokhim., Alma-Ata, USSR
 SO Zh. Prikl. Khim. (Leningrad) (1980), 53(9), 2135-9
 CODEN: ZPKHAB; ISSN: 0044-4618
 DT Journal
 LA Russian
 AB The title process gave 98% linalool acetate using 2.3% Pd/BaSO4 treated with 7.6 times. 10-2 N Na2CO3 as the catalyst in 50% aq. Me2CHOH.
 IT 7440-05-3, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts contg., for hydrogenation of dehydrolinalyl acetate)
 RN 7440-05-3 HCAPLUS
 CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 115-95-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of, by hydrogenation of dehydrolinalyl acetate, catalysts for)
 RN 115-95-7 HCAPLUS
 CN 1,6-Octadien-3-ol, 3,7-dimethyl-, acetate (8CI, 9CI) (CA INDEX NAME)



=> d bib abs hitstr 9

L73 ANSWER 9 OF 9 HCAPLUS COPYRIGHT 2001 ACS

AN 1977:29609 HCAPLUS

DN 86:29609

TI Tetrahydrofuran

IN Smith, William Edward

PA General Electric Co., USA

SO Ger. Offen., 15 pp.

CODEN: GWXXBX

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 2461769	A1	19760701	DE 1974-2461769	19741228
AB	THF was prepd. cheaply and quant. by dehydroacetoxylation of $\text{AcO}(\text{CH}_2)_4\text{OH}$. Thus, propylene, AcOH , O_2 , and H_2O was passed through 0.3% Pd and 3% KOAc on Al ₂ O ₃ at 180.degree., the product $\text{CH}_2\text{:CHCH}_2\text{OAc}$ hydroformylated-hydrogenated with $\text{H}_2\text{-CO}$ and $\text{Co}(\text{CO})_8$, the resultant $\text{AcO}(\text{CH}_2)_3\text{CHO}$ hydrogenated, and the $\text{AcO}(\text{CH}_2)_4\text{OH}$ so obtained cyclized to give 64% THF (based on $\text{CH}_2\text{:CHCH}_2\text{OAc}$).				
IT	7440-05-3, uses and miscellaneous				
	RL: USES (Uses)				
	(potassium acetate and, acetoxylation of propylene in presence of)				
RN	7440-05-3 HCAPLUS				
CN	Palladium (8CI, 9CI) (CA INDEX NAME)				

Pd

IT 591-87-7P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)

(prepn. and hydroformylation-hydrogenation of)

RN 591-87-7 HCAPLUS

CN Acetic acid, 2-propenyl ester (9CI) (CA INDEX NAME)

 $\text{AcO}-\text{CH}_2-\text{CH}=\text{CH}_2$

=> d bib abs 131 1

L31 ANSWER 1 OF 4 HCAPLUS COPYRIGHT 2001 ACS

AN 2001:217747-HCAPLUS

TI Raney metal fixed bed catalyst for
hydrogenation of saturated and unsaturated
esters and the manufacture and use thereofIN Ostgard, Daniel; Berweiler, Monika; Bender, Barbara; Stein, Gernot;
Moebus, Konrad

PA Degussa-Huls A.-G., Germany

SO Jpn. Kokai Tokkyo Koho, 9 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001079410	A2	20010327	JP 2000-229531	20000728
	DE 19936135	A1	20010215	DE 1999-19936135	19990731
PRAI	DE 1999-19936135		19990731		
	US 1999-368571		19990805		

AB The invention relates to the Raney metal fixed bed catalyst from a Raney process metal, a catalyst promoter, a binder, and a wetting agent, wherein the catalyst molded to a certain shape is roasted at .ltoreq.850.degree.; activated by an alk. soln., and dipping it in a soln. contg. perrhenic acid and Rh salts for doping of the catalyst. The catalyst is able to carry out the hydrogenation of maleic acid for the formation of .gamma.-butyrolactone, THF, and 1,4-butanediol at 200.degree. and 80 bar, and has a higher selectivity than a Cu chromite catalyst.

=> d ind

L31 ANSWER 1 OF 4 HCAPLUS COPYRIGHT 2001 ACS

IC ICM B01J025-02

ICS C07C029-149; C07C031-125; C07C031-20; C07D307-08; C07D307-33;

C07B061-00

CC 67-1 (Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms)

Section cross-reference(s): 22

ST Raney metal fixed bed catalyst rhenium doping

IT Hydrogenation

Hydrogenation catalysts

(Raney metal fixed bed catalyst for
hydrogenation of satd. and unsatd. esters)

IT 7440-02-0D, Nickel, doped with rhenium

RL: CAT (Catalyst use); PEP (Physical, engineering or chemical process);

PROC (Process); USES (Uses)

(Raney metal fixed bed catalyst for
hydrogenation of satd. and unsatd. esters)

IT 110-30-5P

RL: PNU (Preparation, unclassified); PREP (Preparation)

(Raney metal fixed bed catalyst for
hydrogenation of satd. and unsatd. esters)

IT 110-16-7, Maleic acid

RL: RCT (Reactant)

(Raney metal fixed bed catalyst for
hydrogenation of satd. and unsatd. esters)IT 96-48-0P, .gamma.-Butyrolactone 109-99-9P, THF 110-63-4P,
1,4-Butanediol

RL: PNU (Preparation, unclassified); PREP (Preparation)

(formation by Raney metal fixed bed catalyst)

IT 7440-15-5, Rhenium 13768-11-1, Perrhenic acid

RL: MOA (Modifier or additive use); USES (Uses)

(prepn. of Raney metal fixed bed catalyst for
hydrogenation of satd. and unsatd. esters)

=> d bib abs 131 2

L31 ANSWER 2 OF 4 HCAPLUS COPYRIGHT 2001 ACS
 AN 1996:410399 HCAPLUS
 DN 125:61478
 TI Hydrogenation of unsaturated fatty acid esters
 IN Darsow, Gerhard Dr
 PA Bayer A.-G., Germany
 SO Eur. Pat. Appl., 8 pp.
 CODEN: EPXXDW
 DT Patent
 LA German
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 709362	A1	19960501	EP 1995-116240	19951016
	EP 709362	B1	19980624		
	R: AT, BE, CH, DE, DK, ES, FR, GB, IT, LI, NL, SE				
	DE 4438547	A1	19960502	DE 1994-4438547	19941028
	AT 167660	E	19980715	AT 1995-116240	19951016
	ES 2117821	T3	19980816	ES 1995-116240	19951016
	US 5861521	A	19990119	US 1995-546344	19951020
	JP 08208562	A2	19960813	JP 1995-297257	19951023
	CA 2161380	AA	19960429	CA 1995-2161380	19951025

PRAI DE 1994-4438547 19941028

AB Esters of C6-30 acids and mono- or divalent C1-20 alcs. are hydrogenated by continuously passing them in a liq. phase through a fixed bed of acid- and carrier-free molded catalyst particles contg. .gtoreq.1 of Fe subgroup of Group VIII elements 65-100, .gtoreq.1 of Group VIB elements 0-15, and .gtoreq.1 hydride of Al, Si, Ti, and C 0-20% with inner surface area 10-90 m²/g and compression strength 20-250 N under 50-350 bar H pressure at 40-150.degree. and 20-60-fold more H than the stoichiometric amt. needed for the esters. This catalyst is useful for .gtoreq.15,000 h, during which the catalyst consumption is <0.1%.

=> d ind 2

L31 ANSWER 2 OF 4 HCAPLUS COPYRIGHT 2001 ACS
 IC ICM C07C067-303
 ICS C11C003-12; C07C069-30
 CC 45-3 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
 Section cross-reference(s): 23, 67
 ST hydrogenation fixed bed catalyst
 unsatd ester; carbonyl powder molded hydrogenation catalyst; titanium hydride powder molded hydrogenation catalyst; silicon hydride powder molded hydrogenation catalyst; aluminum hydride powder molded hydrogenation catalyst; iron powder molded hydrogenation catalyst; continuous hydrogenation unsatd fatty ester
 IT Hydrogenation catalysts
 (continuous hydrogenation of unsatd. fatty acid esters in fixed beds of molded catalysts of metal powders)
 IT Group VIB elements
 RL: CAT (Catalyst use); USES (Uses)
 (continuous hydrogenation of unsatd. fatty acid esters in fixed beds of molded catalysts of metal powders)
 IT Esters, preparation
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (continuous hydrogenation of unsatd. fatty acid esters in fixed beds of molded catalysts of metal powders)
 IT Castor oil
 Rape oil
 Soybean oil
 Sunflower oil
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (hydrogenated, continuous hydrogenation of unsatd. fatty acid esters in fixed beds of molded catalysts of metal powders)
 IT Esters, reactions
 RL: RCT (Reactant)
 (unsatd., continuous hydrogenation of

SEARCHED BY SUSAN HANLEY 305-4053

Page 2

- unsatd. fatty acid esters in fixed
beds of molded catalysts of metal powders)
- IT 7439-89-6, Iron, uses 7440-02-0, Nickel, uses 11102-42-4 51602-58-5
178415-17-3 178415-18-4 178415-19-5 178415-20-8
RL: CAT (Catalyst use); USES (Uses)
(continuous hydrogenation of unsatd. fatty acid
esters in fixed beds of molded catalysts of
metal powders)
- IT 112-61-8P, Methyl stearate
RL: IMF (Industrial manufacture); PREP (Preparation)
(continuous hydrogenation of unsatd. fatty acid
esters in fixed beds of molded catalysts of
metal powders)
- IT 112-63-0, Methyl linoleate
RL: RCT (Reactant)
(continuous hydrogenation of unsatd. fatty acid
esters in fixed beds of molded catalysts of
metal powders)

=> d bib abs 131 3

L31 ANSWER 3 OF 4 HCAPLUS COPYRIGHT 2001 ACS
 AN 1991:43079 HCAPLUS
 DN 114:43079
 TI Catalytic asymmetric hydrogenation by some homogeneous and silica-bound
 .mu.-thiolato-.mu.-chlorodicarbonylbis(neomenthylphenylphosphine)dirhodi-
 um complexes
 AU Eisen, Moris; Blum, Jochanan; Schumann, Herbert; Gorella, Boris
 CS Dep. Org. Chem., Hebrew Univ., Jerusalem, 91904, Israel
 SO J. Mol. Catal. (1989), 56(1-3), 329-37
 CODEN: JMCADS; ISSN: 0304-5102
 DT Journal
 LA English
 OS CASREACT 114:43079
 AB (+)-Dicarbonyl-.mu.-chloro[.mu.-(2-methyl-2-propanethiolato-S:S)]bis{[5-
 methyl-2-(1-methylethyl)cyclohexyl]diphenylphosphine}dirhodium (I) and
 (+)-dicarbonyl-.mu.-chloro[.mu.-(2-triethoxysilyl)ethanethiolato-
 S:S]bis{[5-methyl-2-(1-methylethyl)cyclohexyl]diphenylphosphine}dirhodium
 (II) were prepd. by interaction of (+)-neomenthylphenylphosphine with
 chlorodicarbonylrhodium dimer, followed by treatment of the product with
 the appropriate (alkylthio)trimethylsilane. II was immobilized by
 attachment to silica gel. Both the homogeneous and hybrid catalysts proved
 capable of promoting the asym. hydrogenation of prochiral
 unsatd. acids and esters. While the sol. I and II led
 to the formation of dextro-rotatory products, the recyclable
 supported catalyst gave laevorotatory compds.

=> d bib abs 131 4

L31 ANSWER 4 OF 4 HCAPLUS COPYRIGHT 2001 ACS
 AN 1982:181787 HCAPLUS
 DN 96:181787
 TI Unsaturated acids and esters
 IN Shaw, Wilfrid G.; Rinz, James E.; Pappas, Christos
 PA Standard Oil Co., USA
 SO U.S., 4 pp.
 CODEN: USXXAM
 DT Patent
 LA English
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4307247	A	19811222	US 1980-184591	19800905
	CA 1150732	A1	19830726	CA 1981-378937	19810603
	JP 57050939	A2	19820325	JP 1981-112911	19810717
	EP 47578	A1	19820317	EP 1981-303409	19810724
	EP 47578	B1	19840530		

R: BE, CH, DE, FR, GB, IT, LU, NL, SE
 PRAI US 1980-184591 19800905

AB Satd., lower aliph. acids and esters are oxydehydrogenated to the corresponding unsatd. acids and esters using a catalyst of the formula $M_{0.1-3}P_{0.1-3}Bi_{0.01-2}M_{0.1-3}Cu_{0.01-2}V_{0.01-3}M_{1a}M_{2b}Oc$, where $M = K, Rb, Cs$; $M_1 = Ba, Cd, Ga, Ti, Zn$; $M_2 = Ca, Ce, Co, Cr, Fe, Mg, Ni, Ta, Tl$; $a = 0-2$; $b = 0-2$; and $c = no.$ to satisfy valence requirements of elements present. Thus, $RbOH$ and $Ba(OH)_2$ were added to an aq. soln. of $(NH_4)_6Mo_7O_{24}$ at 30-35.degree.. After 15 min Cu acetate and NH_4VO_3 solns. were added, followed by a $BiCl_3-HCl$ soln. The slurry was heated 2 h at .apprx.70.degree., mixed with H_3PO_4 , and stirred for 30 min. The pH was then adjusted to 5.6, and the mixt. dried to give a powder catalyst precursor ($M_{0.12}PRbBa_{0.2}Bi_{0.25}Cu_{0.25}V_{0.25}Oc$), which was coated on Al_2O_3 spheres. After calcing at 326-370.degree. for 3 h in a downward-flow, fixed-bed reactor, air, water, and isobutyric acid (I) [79-31-2] (I-catalyst vol. ratio 51.6, air-I mol ratio 4.6, and H_2O -I ratio 25.3) were fed into the reactor to give methacrylic acid [79-41-4] in 61.3% yield (91.1% I inversion).

=> d bib abs 113 1

L13 ANSWER 1 OF 6 HCAPLUS COPYRIGHT 2001 ACS

AN 2000:772590 HCAPLUS

DN 133:336867

TI Manufacture of hydrogenated esters,
hydrogenation catalysts for use therein, and preparation
of catalysts

IN Ohga, Kazuhiko; Fujimoto, Masayuki; Uchida, Hiroshi; Tajima, Tsuneo

PA Showa Denko K. K., Japan

SO PCT Int. Appl., 78 pp.

CODEN: PIXXD2

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2000064852	A1	20001102	WO 2000-JP977	20000221
	W:		AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM		
	RW:		GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG		
PRAI	JP 1999-118874		19990427		
	US 1999-141247		19990630		
	JP 1999-193352		19990707		
	US 1999-147812		19990810		
	JP 1999-284520		19991005		
	US 1999-162896		19991101		
OS	MARPAT 133:336867				
AB	A process for highly selectively obtaining a hydrogenated ester from an unsatd. ester comprises hydrogenating the unsatd. ester in an inert solvent using a catalyst contg. at least one metal selected among the elements in Groups 8, 9, and 10 of the Periodic Table.				

RE.CNT 4

RE

- (1) Daicel Chemical Industries Ltd; JP 09194427 A 1997 HCAPLUS
- (2) Mitsubishi Gas Chemical Company Inc; JP 10120605 A 1998 HCAPLUS
- (3) Tosoh Corporation; JP 06279012 A 1994 HCAPLUS
- (4) Ube Industries Ltd; JP 1147597 A 1999

=> d bib abs 113 2

L13 ANSWER 2 OF 6 HCAPLUS COPYRIGHT 2001 ACS
AN 1992:257819 HCAPLUS
DN 116:257819
TI Kinetic and potentiometric studies of the hydrogenation of allyl
esters of some fatty acids
AU Il'khamdzhanov, P.; Mirkamilov, T. M.; Makhmudova, Z.; Makhsumov, A. G.
CS Tashk. Politekh. Inst., Tashkent, USSR
* SO ~~Uzb. Khim. Zh. (1991), (6), 24-7~~
CODEN: UZKZAC; ISSN: 0042-1707
DT Journal
LA Russian
AB The H absorption rate and catalyst potential measured
simultaneously in the liq.-phase, room-temp. hydrogenation of
allyl laurate in the presence of Al-Ni catalysts
modified with different metals (Na, K, Ti, Fe, Cu, Ca), a model reaction
for hydrogenation of allyl esters of fatty
acids, suggested that allyl esters are readily
hydrogenated by these catalysts, although at different
satn. rates. The highest activities, in descending rate order, were
exhibited by catalysts contg. Na, K, and Ti. Catalyst
amts. >1.5 mL per 0.005 g-mol ester did not affect the reaction rate.

Different catalyst
not RCO₂H

no order!

=> d bib abs 113 3

L13 ANSWER 3 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1977:422319 HCAPLUS
 DN 87:22319
 TI Study of the hydrogenation of allyl esters
 of aliphatic acids on different industrial Raney nickel catalysts
 AU Il'khamdzhanov, P.; Makhsumov, A. G.; Makhmudova, Z.; Abdurakhimov, A.
 CS USSR
 SO Deposited Doc. (1975), VINITI 111-75, 8 pp. Avail.: BLLD
 OT Report
 LA Russian
 AB { Ni-Al catalysts contg. Na or K were more active in the hydrogenation of
 allyl laurate than Ni-Al catalysts contg. Ti, Fe, Cu, or Ca. In
 the hydrogenation of allyl caproate the rate increased with
 increasing amt. of catalyst and then leveled off at the same point for
 Ni-Ti-Al, Ni-Fe-Al, and Ni-Cu-Al catalysts.

=> d bib abs 113 4

L13 ANSWER 4 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1976:30354 HCAPLUS
 DN 84:30354
 TI Hydrogenation of the allyl esters of fatty
 acids on industrial catalysts
 AU Makhmudova, Z.; Il'khamdzhanov, I. P.; Abdurakhimov, A.
 CS USSR
 SO Tr. Tashk. Politekh. Inst. (1974), 119, 117-19
 CODEN: TTPLAA
 DT Journal
 LA Russian
 AB The title process in the presence of Raney Ni-Al-Ti (47:50:3) was
 independent of temp. >40.degree.; optimum conditions included MeOH, EtOH,
 hexane, or ligroine as solvent at 20-30.degree..

=> d bib abs 113 5

L13 ANSWER 5 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1975:42692 HCAPLUS
 DN 82:42692
 TI Influence of the catalyst structure on the kinetics of hydrogenation and isomerization
 AU Van der Planck, P.
 CS Unilever Res., Vlaardingen, Neth.
 SO Fette, Seifen, Anstrichm. (1974), 76(8), 337-40
 CODEN: FSASAX
 DT Journal
 LA German
 AB Kinetic studies of the hydrogenation and double bond migration of Me oleate, linoleate, and elaidate, and glyceryl trioleate at 75-129.degree. in the presence of Ni/kieselguhr catalysts of varying (pore) structure showed, that stearate formation was the rate-detg. step in hydrogenation. The double bond migration proceeded faster from the trans- than the cis-position with rate-detg. formation of a .pi.-allyl complex. The results are discussed in terms of oil hardening.

=> d bib abs 113 6

L13 ANSWER 6 OF 6 HCAPLUS COPYRIGHT 2001 ACS
AN 1972:3187 HCAPLUS
DN 76:3187
TI Reactivity of the carbon-carbon double bond of unsaturated esters during
catalytic hydrogenation on a Raney nickel catalyst
AU Freidlin, L. Kh.; Nazarova, N. M.; Rastorgueva, G. A.; Abduraimova, M. A.
CS Inst. Org. Khim. im. Zelinskogo, Moscow, USSR
SO Izv. Akad. Nauk SSSR, Ser. Khim. (1971), (8), 1678-83
CODEN: IASKA6
DT Journal
LA Russian
AB The relative rates of hydrogenation over Ni at 20.degree. were obsd. for
allyl and vinyl esters of the lower fatty acids as well as for
vinyl or allyl alkyl ethers, and Me or Bu esters of acrylic or
methacrylic acids. The rate of reaction was independent of the structure
of the non-unsatd. portion as the intervening O atom prevented its
sorption on the catalyst. The relative adsorption coeffs. and the rates
of hydrogenation of the vinyl derivs. was greater than that for
allyl analogs. The decreased reactivity of vinyl derivs. relative
to the allyl analogs was due to the hindrance caused by the O
atom in adsorption. This explained the greater reactivity of styrene than
PhOCH:CH2.

=> d bib abs hitstr 121 1

L21 ANSWER 1 OF 6 HCAPLUS COPYRIGHT 2001 ACS

AN 1999:565202 HCAPLUS

DN 131:185786

TI Unsaturated polyester-based thermosetting resin compositions for cured products with excellent transparency and heat and weather resistance

IN Matsui, Fumio; Morita, Katsuhisa; Hatano, Yoshitaka; Shimizu, Akihiro

PA Showa Highpolymer Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 6 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 11240923	A2	19990907	JP 1998-43795	19980225
AB	The comps. with good handling and storage stability at an ambient temp. comprise (1) unsatd. polyesters prepd. from polyols (A), satd. polybasic acids (B), and unsatd. polybasic acids (A and/or B is alicyclic compds.), (2) diallyl phthalates, and (3) org. peroxides. Thus, 100 parts of an unsatd. polyester (Mn 3800, Mw 8200, softening temp. 71.3.degree.), which was prepd. from 1,4-cyclohexanedimethanol 144.5, 1,4-cyclohexanedicarboxylic acid 172.0, hydrogenated bisphenol A 243.8, adipic acid 29.2, and fumaric acid 92.8 g, was melt-kneaded with diallyl terephthalate 20, divinylbenzene 3, and dicumyl peroxide 2 parts, pelletized, and transfer-molded to give a test piece showing bending strength 7.5 kg/cm ² , light transmittance 82%, glass-transition temp. 142.degree., and good heat resistance.				

=> d ind

L21 ANSWER 1 OF 6 HCAPLUS COPYRIGHT 2001 ACS

IC ICM C08F283-01

ICS C08K005-14; C08L067-06; C08G063-553; C08F283-01; C08F218-18

CC 37-6 (Plastics Manufacture and Processing)

ST alicyclic unsatd polyester heat resistance; cyclohexanedimethanol

cyclohexanedicarboxylate fumarate unsatd polyester transparency;

allyl terephthalate crosslink unsatd polyester

IT Polyoxyalkylenes, preparation

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(polyester-, unsatd.; unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)

IT Polyesters, preparation

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(polyoxyalkylene-, unsatd.; unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)

IT Heat-resistant materials

Transparent materials

(unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)

IT Polyesters, preparation

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(unsatd.; unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)

IT 240427-42-3P, Adipic acid-1,4-cyclohexanedicarboxylic acid-1,4-cyclohexanedimethanol-diallyl terephthalate-divinylbenzene-fumaric acid-hydrogenated bisphenol A copolymer 240427-43-4P 240427-44-5P

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)

=> d bib abs hitstr 121 2

L21 ANSWER 2 OF 6 HCAPLUS COPYRIGHT 2001 ACS

AN 1998:651099 HCAPLUS

DN 129:303277

TI Unsaturated polyester-thermoplastic resin compositions for cured articles with low thermal expansion and their use in composites with steel

IN Matsui, Fumio; Morita, Katsuhisa; Nakajima, Hiroshi; Hoshino, Toshiaki

PA Showa Highpolymer Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 8 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN. CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 10265662	A2	19981006	JP 1997-72142	19970325

AB The compns. comprise unsatd. polyesters, diallyl phthalates, thermoplastic resins having glass transition temp. (Tg) .ltoreq.150.degree., polymn. initiators, and inorg. fillers and their cured articles show cure shrinkage .ltoreq.0.1% and thermal expansion coeff. at room temp.-300.degree. 0.7 .times. 10-5-1.5 .times. 10-5/.degree.C. The composites consisting of the polymer compns. and steel are also claimed. Thus, a mixt. contg. 1,4-butanediol-dimethyl terephthalate-fumaric acid copolymer, diallyl terephthalate, polystyrene, styrene monomer, dicumyl peroxide, SiO2 powders, and microcapsulated red P was press-molded and cured to give a test piece showing cure shrinkage 0.05%, Tg 308.degree., linear thermal expansion coeff. at 100.degree. 0.9 .times. 10-5/.degree.C, and flammability rating V-0.

=> d bib abs hitstr 121 3

L21 ANSWER 3 OF 6 HCAPLUS COPYRIGHT 2001 ACS

AN 1993:541378 HCAPLUS

DN 119:141378

TI Unsaturated polyester compositions and their use as binders in putty

IN Fujishima, Minoru

PA Hitachi Chemical Co Ltd, Japan

SO Jpn. Kokai Tokkyo Koho, 7 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 05078459	A2	19930330	JP 1991-240105	19910920
AB	<p>Title compns., applicable to zinc-treated anticorrosive steel sheets to form heat shock- and moisture-resistant films with good adhesion and polishing quality and useful for automobile repair, comprise 30-80% unsatd. polyesters obtained from polybasic acids contg. 0-90 mol% satd. acids and 10-100 mol% .alpha.,.beta.-unsatd. acids and polyhydric alcs. contg. 20-60 mol% hydrogenated bisphenol A and 10-40 mol% allyl glycidyl ether at alcs./acids = 1.0-2.0 (mol) and 20-70% liq. polymerizable compds. Thus, a mixt. of Rikabinol HB 813.6, diethylene glycol 239.7, maleic anhydride 553.7, and hydroquinone 0.2 part was heated in xylene, then heated with 193.2 parts Epiol A in the presence of Cation M2-100 (dimethyldodecylbenzylammonium chloride) to give an unsatd. polyester, which was dild. with styrene contg. hydroquinone. A putty contg. the unsatd. polyester compns., diethylaniline, Co naphthenates, .alpha.-naphthoquinone (stabilizer), TiO₂, and talc was mixed with MEK peroxide, applied to a galvanized iron sheet at 2-mm thickness, and dried at 20.degree. for 14 min to form a film, which was polishable after 4 h and showed good adhesion and resistance to moisture and 4 heat cycles (80.degree./2 h .dblarw. -20.degree./2 h).</p>				

=> d bib abs hitstr 121 4

L21 ANSWER 4 OF 6 HCAPLUS COPYRIGHT 2001 ACS

AN 1992:7470 HCAPLUS

DN 116:7470

TI Unsaturated polyester molding materials with high flash point and low shrinkage

IN Kubo, Toshio; Sawano, Shin

PA Matsushita Electric Works, Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN. CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 03192108	A2	19910822	JP 1989-331538	19891221

AB The title materials comprise unsatd. polyesters, diallyl phthalate (I), thermoplastic resins, and styrene. Thus, with 80 parts 70:30 mixt. of hydrogenated bisphenol-based unsatd. polyester and I was blended a 30:70 polystyrene-styrene mixt. 20, BPO 1, Zn stearate 7, CaCO₃ 300, and glass fibers 75 parts and then hot pressed at 100 kg/cm² and 160.degree. for 90 s to give a molding with flash point 59.degree. and shrinkage 0.31%, vs. .gtoreq.100 and 0.38, resp., for a control without polystyrene-styrene mixt.

=> d bib abs hitstr 121 5

L21 ANSWER 5 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1991:145647 HCAPLUS
 DN 114:145647
 TI Radiation-curable resin compositions containing modified cyclopentadiene
 polymers as binders for inks and coatings
 IN Suzuki, Akinori; Sasaki, Makoto; Tsucha, Shozo
 PA Nippon Oil Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 9 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN. CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 02215805	A2	19900828	JP 1989-36356	19890217
GI					



Rn I

AB The title compns. contain 10-95 parts diluents and 5-90 parts curable
 resins prepd. by thermal polymn. of 100 parts cyclopentadienes I (R = C1-3
 alkyl; n = 0-6) and/or their Diels-Alder adducts with 0-50 parts arom.
 olefins and 2-120 parts pentaerythritol di- or triallyl ether or
 trimethylolpropane diallyl ether and esterifying the resulting OH-contg.
 resins and/or their hydrogenated derivs. with .alpha.,.beta.-unsatd.
 carboxylic acids at acid/OH equiv ratio 0.1-1.1 after optional treatment
 of part of OH with polyisocyanates, polycarboxylic acids, or their esters.
 Thus, polymg. dicyclopentadiene 700, pentaerythritol allyl ether 210, and
 pentaerythritol diallyl ether 90 g in xylene at 260.degree. for 3 h and
 esterifying 100 g of the resulting resin (OH value 0.135 mol/100 g) with
 10.7 g acrylic acid in benzene-MIBK mixt. in presence of p-MeC6H4SO3H and
 hydroquinone at 100.degree. for 14 h gave a resin. An ink contg. the
 resin 32, trimethylolpropane triacrylate 44, Carmine 6B 17, Irgacure 184
 7, and hydroquinone 0.1 part showed UV curing time 3 s, good gloss, and
 excellent misting resistance.

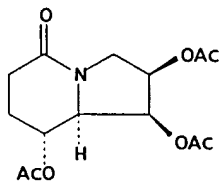
=> d bib abs hitstr 121 6

L21 ANSWER 6 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1975:141718 HCAPLUS
 DN 82:141718
 TI Unsaturated polyester compositions
 IN Miyawaki, Takeshi; Yutani, Seisuke; Takahama, Yoshio; Nikki, Masao
 PA Japan Catalytic Chemical Industry Co., Ltd.
 SO Japan. Kokai, 8 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 49130989	A2	19741216	JP 1973-44062	19730420
	JP 52039634	B4	19771006		
AB	<p>Unsatd. polyesters (20-80 parts) were mixed with 20-80 parts crosslinking agents [65-99 wt.% styrene (I) [100-42-5], chlorostyrene, and(or) vinyltoluene and 1-35 wt.% diallyl phthalate (II) [131-17-9], diallyl isophthalate, triallyl cyanurate, triallyl isocyanurate, and(or) acrylates or methacrylates (b. >200.degree.))] and hardened to give smooth coatings with improved luster. Thus, maleic anhydride 980, trimethylolpropane diallyl ether 449, ethylene glycol 586, and a partially esterified product of a 1:1 hydrogenated rosin-trimethylolpropane mixt. 456 parts were polymd. at 180.degree. in N; a mixt. of the unsatd. polyester (acid no. 17)(100 parts), 10 parts II, and 100 parts I was mixed with 1 wt.% cumene hydroperoxide and 0.5 wt.% Co octenate, spray-coated (300.mu. thickness) on a laminated panel, and hardened 7 min at 80.degree. to give a pinhole-free coating.</p>				

REYES 09/582,495

RX(26) OF 468

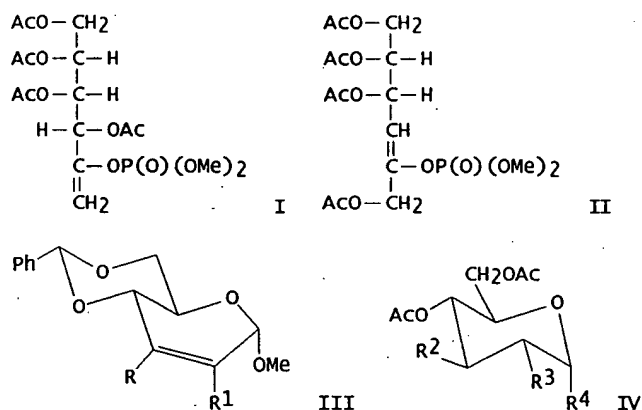


REF: Carbohydr. Res., 136, 225-40; 1985

OF 11 CASREACT COPYRIGHT 2001 ACS

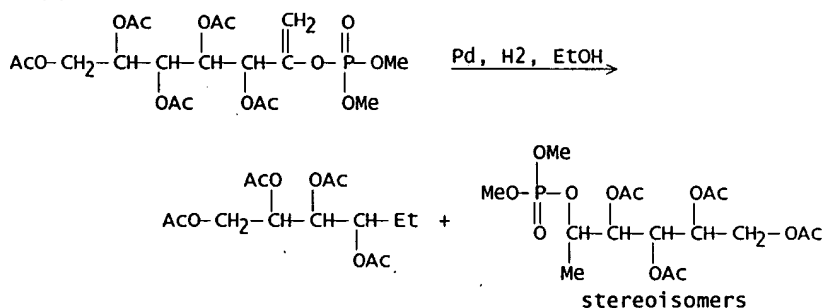
=> d bib abs fcrdref 11

L45 ANSWER 11 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 103:22851 CASREACT
 TI Studies of hydrogenation of saccharide enol phosphates
 AU Thiem, Joachim; Rasch, Dieter
 CS Org.-Chem. Inst., Univ. Muenster, Muenster, D-4400, Fed. Rep. Ger.
 SO Liebigs Ann. Chem. (1985), (3), 536-44
 CODEN: LACHDL; ISSN: 0170-2041
 DT Journal
 LA German
 GI



AB Hydrogenation of the isomeric acyclic enol phosphates I and II in the presence of Pd/C gave predominantly epimeric deoxy phosphates. Similar hydrogenation of pyranoid enol phosphate III [R = H, R1 = OP(O)(OMe)2] followed by acetylation gave hexopyranoside IV [R2 = H, R3 = OP(O)(OMe)2, R4 = OMe], while III [R = OP(O)(OMe)2, R1 = H] gave anhydro product [IV; R2 = OP(O)(OMe)2, R3 = R4 = H]. Hydrogenation of Me 5-O-benzoyl-2-deoxy-3-O-(dimethoxyphosphoryl)-.beta.-D-glycero-pent-2-enofuranoside gave 1,4-anhydro-5-O-benzoyl-2,3-dideoxy-D-glycero-pentitol.

RX(1) OF 35



REF: Liebigs Ann. Chem., (3), 536-44; 1985

OF 11 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 159 1

L59 ANSWER 1 OF 7 CASREACT] COPYRIGHT 2001 ACS

AN 119:116733 CASREACT

TI The reaction of perfluoroalkanesulfinates. VII. Fenton reagent-initiated addition of sodium perfluoroalkanesulfinates to alkenes

AU Huang, Weiyuan; Lu, Long

CS Shanghai Inst. Org. Chem., Chin. Acad. Sci., Shanghai, 200032, Peop. Rep. China

SO Chin. J. Chem. (1992), 10(4), 365-72

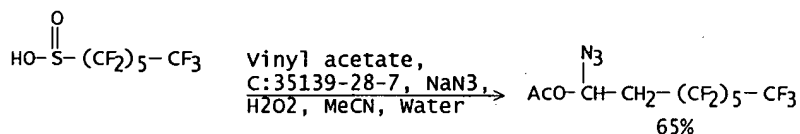
CODEN: CJOCEV

DT Journal

LA English

AB Addn. of sodium perfluoroalkanesulfinates, e.g., RSO_2Na [$\text{R} = \text{Cl}(\text{CF}_2)_4$, $\text{Cl}(\text{CF}_2)_6$, $\text{CF}_3(\text{CF}_2)_5$], to terminal olefins, e.g., $\text{CH}_2:\text{CHR}_1$ [$\text{R}_1 = \text{Bu}$, hexyl, octyl, OAc , CH_2OAc , $(\text{CH}_2)_8\text{CO}_2\text{Et}$], initiated by Fenton reagent ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in the presence of NaN_3 gave adducts $\text{RCH}_2\text{CHN}_3\text{R}_1$ in 50-70% yields. A radical mechanism was proposed based on EPR studies and other evidence. The adducts were readily reduced to amines $\text{RCH}_2\text{CH}(\text{NH}_2)\text{R}_1$ via catalytic hydrogenation. The reactions afford a convenient and effective route to these organofluorine compds.

RX(3) OF 10



Na

REF: Chin. J. Chem., 10(4), 365-72; 1992

NOTE: <20.degree.

OF 7 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcdref 159 2

L59 ANSWER 2 OF 7 CASREACT COPYRIGHT 2001 ACS

AN 112:179088 CASREACT

TI Selectivities in organic reactions via .pi.-allylpalladium complexes

AU Tsuji, Jiro

CS Tokyo Inst. Technol., Tokyo, 152, Japan

SO Pure Appl. Chem. (1989), 61(10), 1673-80

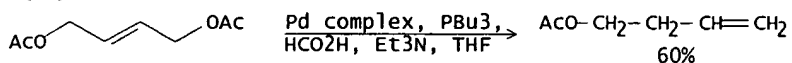
CODEN: PACHAS; ISSN: 0033-4545

DT Journal

LA English

AB Studies on regio- and stereoselectivities in the reactions of allylic carbonates and 2-vinylloxiranes with various nucleophiles were carried out in the presence of a Pd catalyst. It was found that the introduction of a trimethylsilyl group to allyl systems showed a profound effect on the regioselectivity. Terminal allylic carbonates and acetates were converted to 1-alkenes from reaction with HCO₂H-Et₃N in the presence of Pd catalyst.

RX(18) OF 29

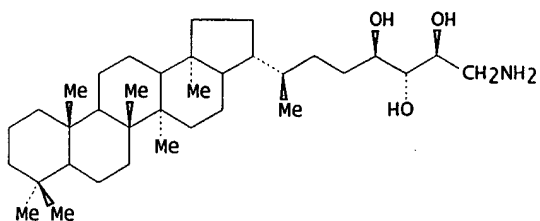


REF: Pure Appl. Chem., 61(10), 1673-80; 1989

OF 7 CASREACT COPYRIGHT 2001 ACS

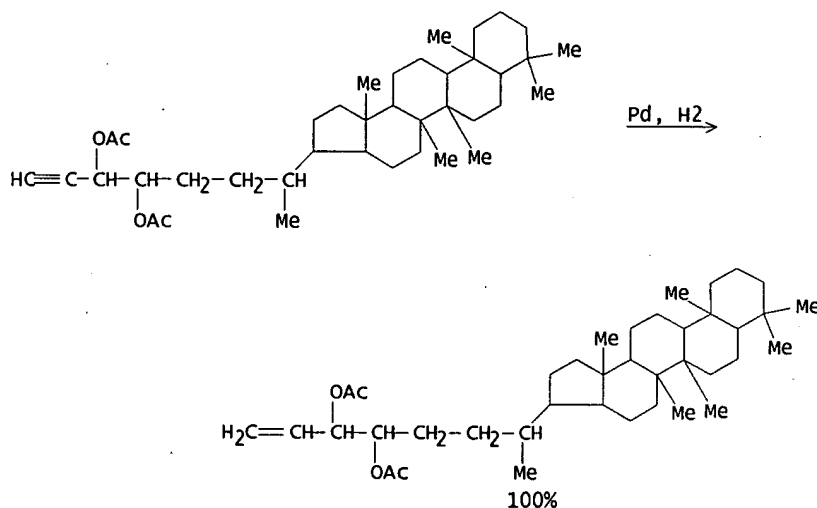
=> d bib abs fcrdref 159 3

L59 ANSWER 3 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 111:154169 CASREACT
 TI A convenient route to an acetylenic C35 hopanoid and the absolute configuration of the side-chain of aminobacteriohopanetriol
 AU Neunlist, Serge; Rohmer, Michel
 CS Ec. Natl. Super. Chim., Mulhouse, F-68093, Fr.
 SO J. Chem. Soc., Chem. Commun. (1988), (12), 830-2
 CODEN: JCCCAT; ISSN: 0022-4936
 DT Journal
 LA English
 GI



AB The abs. configuration of the side chain of aminobacteriohopanetriol I was detd. as 32R,33R,34S by NMR of its 32,34-o-isopropylidene-N-acetyl deriv. and by chem. correlation with bacteriohopanetetrol yielding an acetylenic bacteriophane intermediate of potential synthetic value.

RX(7) OF 24



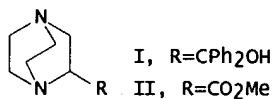
REF: J. Chem. Soc., Chem. Commun., (12), 830-2; 1988

NOTE: Lindlar catalyst

OF 7 CASREACT COPYRIGHT 2001 ACS

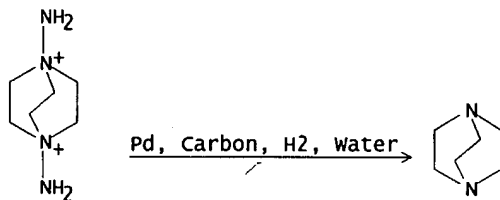
=> d bib abs fcdref 159 4

L59 ANSWER 4 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 111:115134 CASREACT
 TI Synthesis and pharmacological study of 4-azaanalog of phencarol
 AU Yakhontov, L. N.; Kutina, N. N.; Shishkin, G. V.; Zhikhareva, G. P.;
 Vysochin, V. I.; Vorob'eva, V. Ya.; Kaminka, M. E.; Shevchenko, I. L.;
 Mashkovskii, M. D.
 CS VNIKhFI im. Ordzhonikidze, Moscow, USSR
 SO Khim.-Farm. Zh. (1989), 23(1), 30-5
 CODEN: KHFZAN; ISSN: 0023-1134
 DT Journal
 LA Russian
 GI



AB 2-(1,4-Diazabicyclo[2.2.2]octyl)diphenylcarbinol (I), the aza analog of the unique antiallergic agent phencarol was prepd. from II. A pharmacol. study showed that the change in the structure of phencarol by inserting the second atom of nitrogen into position 4 of the quinuclidine nucleus led to decrease in antiallergic and antiinflammatory activities, increase in toxicity, and appearance of a sedative effect of the drug.

RX(8) OF 38

2 Br⁻

REF: Khim.-Farm. Zh., 23(1), 30-5; 1989

OF 7 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 159 5

L59 ANSWER 5 OF 7 CASREACT COPYRIGHT 2001 ACS

AN 111:38589 CASREACT

TI Palladium(0)-catalyzed azidation of allyl esters.

Selective synthesis of allyl azides, primary allyl amines, and related compounds

AU Murahashi, Shunichi; Taniguchi, Yuki; Imada, Yasushi; Tanigawa, Yoshio

CS Fac. Eng. Sci., Osaka Univ., Toyonaka, 560, Japan

SO J. Org. Chem. (1989), 54(14), 3292-303

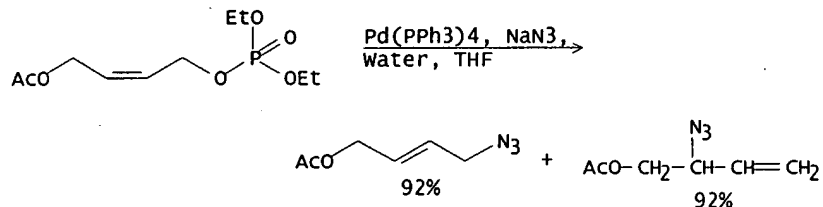
CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

AB Palladium(0)-catalyzed reaction of allyl esters such as phosphates, carbonates, and carboxylates with NaN₃ gives allyl azides. The azidation proceeds with retention of configuration at the allylic carbon. Optically active (R)-(E)-(+)-4-phenyl-3-buten-2-yl azide is obtained from (R)-(E)-(+)-4-phenyl-3-buten-2-yl acetate stereoselectively. Sequential substitution of (Z)-4-acetoxy-2-buten-1-yl di-Et phosphate with nucleophiles and subsequently azide ion gives (E)-4-substituted 2-buten-1-yl azides. The reaction of allyl azides with Ph₃P gives iminotriphenylphosphoranes, which are versatile synthetic intermediates of primary allyl amines, N-allyl imines, and N-allyl amides. Treatment of allyl azides with Ph₃P and subsequently with aq. ammonium soln. gives primary allyl amines. Other synthetic applications of allyl azides are also described.

RX(29) OF 107



REF: J. Org. Chem., 54(14), 3292-303; 1989

NOTE: Safety

OF 7 CASREACT COPYRIGHT 2001 ACS

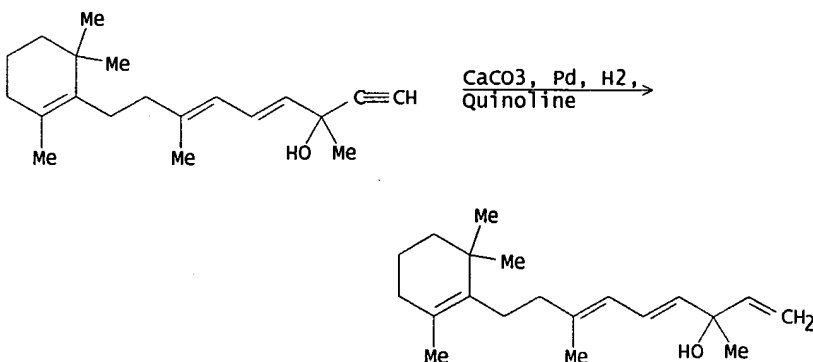
=> d bib abs fcdref 159 6

L59 ANSWER 6 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 105:43110 CASREACT
 TI Oxybromination of polyene alcohols with N-bromosuccinimide
 AU Tutorskaya, O. O.; Miropol'skaya, M. A.; Brodskii, A. V.; Samokhvalov, G. I.
 CS Nauchno-Proizvod. Ob'edin. "Vitaminy", Moscow, USSR
 SO Zh. Org. Khim. (1985), 21(9), 1840-5
 CODEN: ZORKAE; ISSN: 0514-7492
 DT Journal
 LA Russian
 GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Oxybromination of the isomeric vinyl carbinols I and II (R = H) and their acetates (R = Ac) by N-bromosuccinimide gave 61 and 64% bromo alcs. III and IV, which were dehydrobrominated by K₂CO₃ to give 83% diol V and 87% epoxide VI. A mechanism involving ionic addn. of Br and OH to the polyene chain is proposed.

RX(5) OF 33

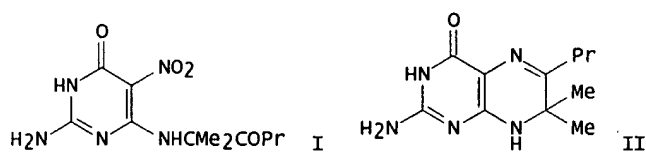


REF: Zh. Org. Khim., 21(9), 1840-5; 1985
 NOTE: petroleum ether solvent

OF 7 CASREACT COPYRIGHT 2001 ACS

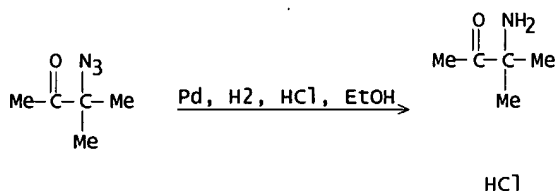
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L59 ANSWER 7 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 104:168438 CASREACT
 TI Specific inhibitors in vitamin biosynthesis. Part 7. Syntheses of
 blocked 7,8-dihydropteridines via .alpha.-amino ketones
 AU Al-Hassan, Saiba S.; Cameron, Robert J.; Curran, Adrian W. C.; Lyall,
 William J. S.; Nicholson, Sydney H.; Robinson, David R.; Stuart,
 Alexander; Suckling, Colin J.; Stirling, Irene; Wood, Hamish C. S.
 CS Dep. Pure Appl. Chem., Univ. Strathclyde, Glasgow, G1 1XL, UK
 SO J. Chem. Soc., Perkin Trans. 1 (1985), (8), 1645-59
 CODEN: JCPRB4; ISSN: 0300-922X
 DT Journal
 LA English
 GI



AB Fifteen blocked 7,8-dihydropteridines were prepd.; the pyrazine ring was built from an .alpha.-amino ketone. E.g., reaction of $\text{PrCOCMe}_2\text{NH}_3^+ \text{Cl}^-$ with 2-amino-6-chloro-5-nitropyrimidin-4(3H)-one in refluxing EtOH contg. Et₃N for 24 h gave 55% pyrimidine I, which on treatment with NaOH and Na₂S₂O₄ in H₂O gave 91% pteridine II. Three routes to the amino ketones based on amino acids, NOCl addn. to alkenes, and nitro alcs. are discussed. These compds. are inhibitors of 6-hydroxymethyl-7,8-dihydropterin pyrophosphokinase, an enzyme in the path to dihydrofolate, and their inhibitory potencies are discussed in the light of a hypothetical active site model for the enzyme.

RX(19) OF 582



REF: J. Chem. Soc., Perkin Trans. 1, (8), 1645-59; 1985

OF 7 CASREACT COPYRIGHT 2001 ACS

=> d ind 7

L59 ANSWER 7 OF 7 CASREACT COPYRIGHT 2001 ACS
 CC 28-17 (Heterocyclic Compounds (More Than One Hetero Atom))
 Section cross-reference(s): 7, 23
 ST pteridine prepn hydroxymethylpterin pyrophosphokinase inhibition; amino
 ketone prepn pteridine precursor
 IT coupling reaction
 (of aminochloronitropyridinone with amino ketones, in prepn. of blocked
 dihydropteridines)
 IT ketones, reactions
 RL: RCT (Reactant)
 (amino, coupling reactions of, with aminochloronitropyrimidinone, in
 prepn. of blocked dihydropteridines)
 IT cyclocondensation reaction
 (intramol., of [(oxoalkyl)amino]nitroaminopyrimidinones, blocked
 dihydropteridines by)
 IT 96-22-0 108-94-1, reactions 2550-26-7
 RL: RCT (Reactant)
 (Wittig reaction of, with tri-Et phosphonoacetate)
 IT 867-13-0
 RL: RCT (Reactant)
 (Wittig reactions of, with ketones)
 IT 556-82-1 591-49-1 693-89-0 1191-16-8
 RL: RCT (Reactant)
 (addn. reaction of, with nitrosyl chloride)
 IT 2648-71-7
 RL: RCT (Reactant)
 (azidation of)
 IT 62-57-7
 RL: RCT (Reactant)
 (condensation reaction of, with phthalic anhydride)
 IT 85-44-9
 RL: RCT (Reactant)
 (condensation reactions of, with amino carboxylic acids)
 IT 36848-04-1 101232-03-5
 RL: RCT (Reactant)
 (coupling reaction of, with aminochloronitropyrimidinone)
 IT 64298-85-7
 RL: RCT (Reactant)
 (hydrolysis of)
 IT 50936-55-5
 RL: PROC (Process)
 (inhibition of, by blocked dihydropterins)
 IT 1194-21-4
 RL: RCT (Reactant)
 (nitration of)
 IT 20575-38-6
 RL: RCT (Reactant)
 (oxidn. and redn. of)
 IT 20570-67-6 20570-69-8
 RL: RCT (Reactant)
 (oxidn. of)
 IT 14463-79-7P 101210-79-1P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and acid chloride formation of)
 IT 932-89-8P 39821-65-3P 55066-44-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and addn. reaction of, with nitrosyl chloride)
 IT 64282-11-7P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and amidation of, with phthalic anhydride)
 IT 4545-04-4P 88934-90-1P 101210-86-0P 101210-87-1P 101210-88-2P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and amination of)
 IT 32211-90-8P 101210-83-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and amine deprotection of)
 IT 13325-14-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and benzoylation of)
 IT 10201-10-2P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and catalytic hydrogenation of)

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Page 8

- IT 10201-16-8P 52312-36-4P 52312-37-5P 53931-60-5P 101210-85-9P
 101210-92-8P 101210-93-9P 101210-97-3P 101210-98-4P 101231-99-6P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and coupling reaction of, with aminochloronitropyrimidinone)
- IT 1007-99-4P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and coupling reactions of, with amino ketones, in prepn. of
 dihydropteridines)
- IT 32211-88-4P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and diazotization of)
- IT 86208-79-9P 101210-96-2P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and hydrogenation of)
- IT 32211-89-5P 37557-72-5P 101210-78-0P 101210-99-5P 101211-10-3P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and hydrolysis of)
- IT 10201-21-5P 37557-79-2P 52312-39-7P 52479-24-0P 53640-85-0P
 101211-01-2P 101211-06-7P 101211-14-7P 101211-15-8P 101224-20-8P
 101224-21-9P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and inhibition by, of hydroxymethyldihydropterin
 pyrophosphokinase)
- IT 10201-18-0P 37557-75-8P 52312-38-6P 52403-64-2P 101211-00-1P
 101211-02-3P 101211-04-5P 101211-05-6P 101211-07-8P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and intramol. cyclocondensation of, dihydropteridinone by)
- IT 101211-11-4P 101211-13-6P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and intramol. cyclocondensation reaction of, dihydropteridinone
 by)
- IT 37557-71-4P 101232-01-3P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and oxidn. of)
- IT 15249-93-1P 34188-63-1P 55591-26-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and redn. of)
- IT 10201-15-7P 13292-96-1P 32211-91-9P 101210-84-8P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and semicarbazone formation of)
- IT 32211-92-0P 53640-81-6P 101210-82-6P 101210-89-3P 101210-91-7P
 101210-94-0P 101210-95-1P 101211-08-9P 101211-16-9P 101211-17-0P
 101232-00-2P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of)
- IT 101210-90-6P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., amination, and coupling reaction of, with
 aminochloronitropyrimidinone)
- IT 101210-81-5P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., chlorination, and hydrolysis of)
- IT 101210-80-4P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., diazotization, and chlorination of)
- IT 101232-02-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn., hydrolysis, and intramol. cyclocondensation of,
 dihydropteridinone by)
- IT 101211-03-4P 101211-09-0P 101211-12-5P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., oxidn., and inhibitory activity of, towards
 hydroxymethyldihydropterin pyrophosphokinase)

=> d bib abs fcrdref 159 1

L59 --ANSWER=1-OF-7--CASREACT] COPYRIGHT 2001 ACS

AN 119:116733 CASREACT

TI The reaction of perfluoroalkanesulfinates. VII. Fenton reagent-initiated addition of sodium perfluoroalkanesulfinates to alkenes

AU Huang, Weiyuan; Lu, Long

CS Shanghai Inst. Org. Chem., Chin. Acad. Sci., Shanghai, 200032, Peop. Rep. China

SO Chin. J. Chem. (1992), 10(4), 365-72

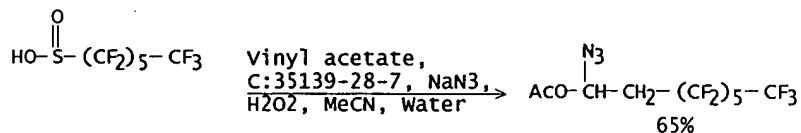
CODEN: CJOCEV

DT Journal

LA English

AB Addn. of sodium perfluoroalkanesulfinates, e.g., RSO_2Na [$\text{R} = \text{Cl}(\text{CF}_2)_4$, $\text{Cl}(\text{CF}_2)_6$, $\text{CF}_3(\text{CF}_2)_5$], to terminal olefins, e.g., $\text{CH}_2:\text{CHR}_1$ [$\text{R}_1 = \text{Bu}$, hexyl, octyl, OAc , CH_2OAc , $(\text{CH}_2)_8\text{CO}_2\text{Et}$], initiated by Fenton reagent ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in the presence of NaN_3 gave adducts $\text{RCH}_2\text{CHN}_3\text{R}_1$ in 50-70% yields. A radical mechanism was proposed based on EPR studies and other evidence. The adducts were readily reduced to amines $\text{RCH}_2\text{CH}(\text{NH}_2)\text{R}_1$ via catalytic hydrogenation. The reactions afford a convenient and effective route to these organofluorine compds.

RX(3) OF 10



REF: Chin. J. Chem., 10(4), 365-72; 1992

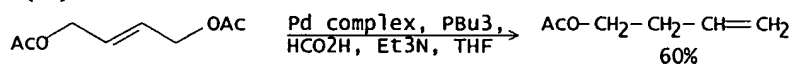
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OF 7 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 159 2

L59 ANSWER 2 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 112:179088 CASREACT
 TI Selectivities in organic reactions via π -allylpalladium complexes
 AU Tsuji, Jiro
 CS Tokyo Inst. Technol., Tokyo, 152, Japan
 SO Pure Appl. Chem. (1989), 61(10), 1673-80
 CODEN: PACHAS; ISSN: 0033-4545
 DT Journal
 LA English
 AB Studies on regio- and stereoselectivities in the reactions of allylic carbonates and 2-vinylloxiranes with various nucleophiles were carried out in the presence of a Pd catalyst. It was found that the introduction of a trimethylsilyl group to allyl systems showed a profound effect on the regioselectivity. Terminal allylic carbonates and acetates were converted to 1-alkenes from reaction with $\text{HCO}_2\text{H}-\text{Et}_3\text{N}$ in the presence of Pd catalyst.

RX(18) OF 29

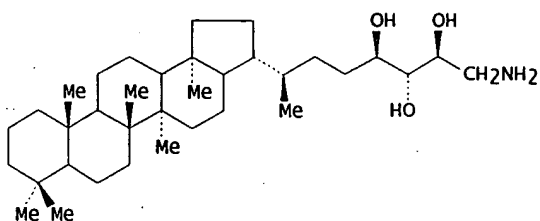


REF: Pure Appl. Chem., 61(10), 1673-80; 1989

OF 7 CASREACT COPYRIGHT 2001 ACS

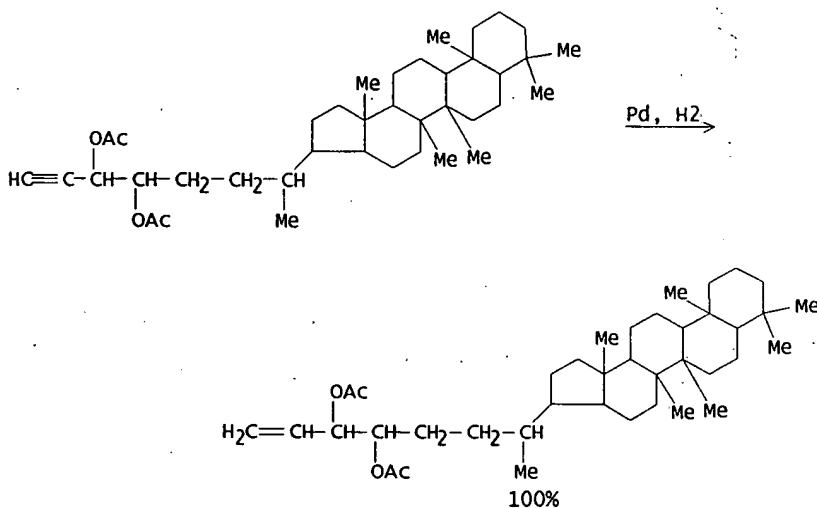
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L59 ANSWER 3 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 111:154169 CASREACT
 TI A convenient route to an acetylenic C35 hopanoid and the absolute configuration of the side-chain of aminobacteriohopanetriol
 AU Neunlist, Serge; Rohmer, Michel
 CS Ec. Natl. Super. Chim., Mulhouse, F-68093, Fr.
 SO J. Chem. Soc., Chem. Commun. (1988), (12), 830-2
 CODEN: JCCCAT; ISSN: 0022-4936
 DT Journal
 LA English
 GI



AB The abs. configuration of the side chain of aminobacteriohopanetriol I was detd. as 32R,33R,34S by NMR of its 32,34-o-isopropylidene-N-acetyl deriv. and by chem. correlation with bacteriohopanetetrol yielding an acetylenic bacteriophane intermediate of potential synthetic value.

RX(7) OF 24



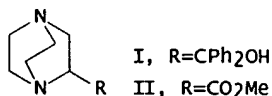
REF: J. Chem. Soc., Chem. Commun., (12), 830-2; 1988

NOTE: Lindlar catalyst

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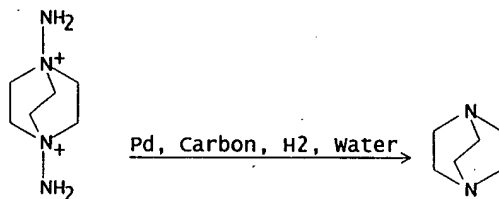
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L59 ANSWER 4 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 111:115134 CASREACT
 TI Synthesis and pharmacological study of 4-azaanalog of phencarol
 AU Yakhontov, L. N.; Kutina, N. N.; Shishkin, G. V.; Zhikhareva, G. P.;
 Vysochin, V. I.; Vorob'eva, V. Ya.; Kaminka, M. E.; Shevchenko, I. L.;
 Mashkovskii, M. D.
 CS VNIKhFI im. Ordzhonikidze, Moscow, USSR
 SO Khim.-Farm. Zh. (1989), 23(1), 30-5
 CODEN: KHFZAN; ISSN: 0023-1134
 DT Journal
 LA Russian
 GI



AB 2-(1,4-Diazabicyclo[2,2,2]octyl)diphenylcarbinol (I), the aza analog of the unique antiallergic agent phencarol was prepd. from II. A pharmacol. study showed that the change in the structure of phencarol by inserting the second atom of nitrogen into position 4 of the quinuclidine nucleus led to decrease in antiallergic and antiinflammatory activities, increase in toxicity, and appearance of a sedative effect of the drug.

RX(8) OF 38

2 Br⁻

REF: Khim.-Farm. Zh., 23(1), 30-5; 1989

OF 7 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 159 5

L59 ANSWER 5 OF 7 CASREACT COPYRIGHT 2001 ACS

AN 111:38589 CASREACT

TI Palladium(0)-catalyzed azidation of allyl esters.
Selective synthesis of allyl azides, primary allylamines, and related compounds

AU Murahashi, Shunichi; Taniguchi, Yuki; Imada, Yasushi; Tanigawa, Yoshio

CS Fac. Eng. Sci., Osaka Univ., Toyonaka, 560, Japan

SO J. Org. Chem. (1989), 54(14), 3292-303

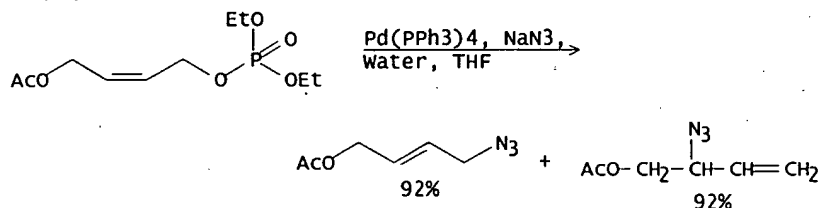
CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

AB Palladium(0)-catalyzed reaction of allyl esters such as phosphates, carbonates, and carboxylates with NaN₃ gives allyl azides. The azidation proceeds with retention of configuration at the allylic carbon. Optically active (R)-(E)-(+)-4-phenyl-3-buten-2-yl azide is obtained from (R)-(E)-(+)-4-phenyl-3-buten-2-yl acetate stereoselectively. Sequential substitution of (Z)-4-acetoxy-2-buten-1-yl di-Et phosphate with nucleophiles and subsequently azide ion gives (E)-4-substituted 2-buten-1-yl azides. The reaction of allyl azides with Ph₃P gives iminotriphenylphosphoranes, which are versatile synthetic intermediates of primary allylamines, N-allyl imines, and N-allyl amides. Treatment of allyl azides with Ph₃P and subsequently with aq. ammonium soln. gives primary allylamines. Other synthetic applications of allyl azides are also described.

RX(29) OF 107



REF: J. Org. Chem., 54(14), 3292-303; 1989

NOTE: Safety

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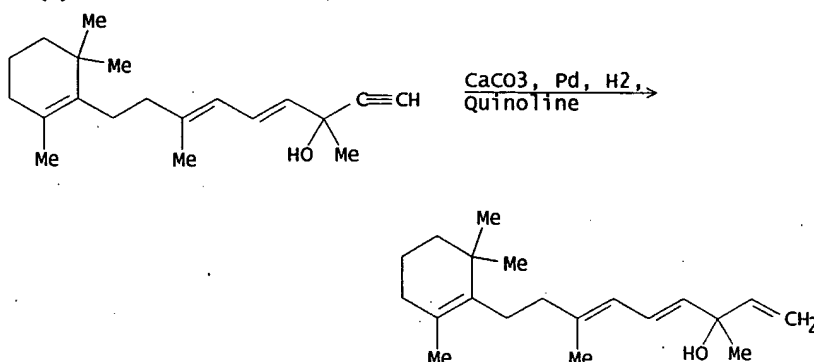
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L59 ANSWER 6 OF 7 CASREACT COPYRIGHT 2001 ACS
 AN 105:43110 CASREACT
 TI Oxybromination of polyene alcohols with N-bromosuccinimide
 AU Tutorskaya, O. O.; Miropol'skaya, M. A.; Brodskii, A. V.; Samokhvalov, G. I.
 CS Nauchno-Proizvod. Ob'edin. "Vitaminy", Moscow, USSR
 SO Zh. Org. Khim. (1985), 21(9), 1840-5
 CODEN: ZORKAE; ISSN: 0514-7492
 DT Journal
 LA Russian
 GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Oxybromination of the isomeric vinyl carbinols I and II (R = H) and their acetates (R = Ac) by N-bromosuccinimide gave 61 and 64% bromo alcs. III and IV, which were dehydrobrominated by K₂CO₃ to give 83% diol V and 87% epoxide VI. A mechanism involving ionic addn. of Br and OH to the polyene chain is proposed.

RX(5) OF 33



REF: Zh. Org. Khim., 21(9), 1840-5; 1985
 NOTE: petroleum ether solvent

OF 7 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 159 7

L59 ANSWER 7 OF 7 CASREACT COPYRIGHT 2001 ACS

AN 104:168438 CASREACT

TI Specific inhibitors in vitamin biosynthesis. Part 7. Syntheses of blocked 7,8-dihydropteridines via .alpha.-amino ketones

AU Al-Hassan, Saiba S.; Cameron, Robert J.; Curran, Adrian W. C.; Lyall, William J. S.; Nicholson, Sydney H.; Robinson, David R.; Stuart, Alexander; Suckling, Colin J.; Stirling, Irene; Wood, Hamish C. S.

CS Dep. Pure Appl. Chem., Univ. Strathclyde, Glasgow, G1 1XL, UK

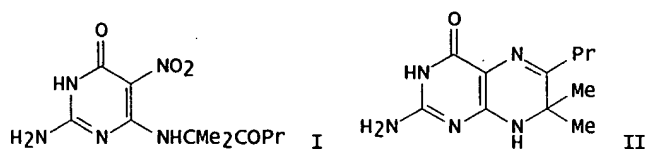
SO J. Chem. Soc., Perkin Trans. 1 (1985), (8), 1645-59

CODEN: JCPRB4; ISSN: 0300-922X

DT Journal

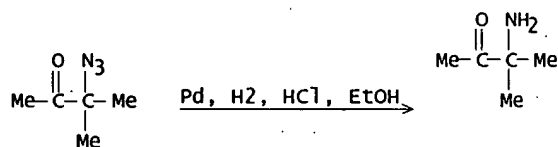
LA English

GI



AB Fifteen blocked 7,8-dihydropteridines were prepd.; the pyrazine ring was built from an .alpha.-amino ketone. E.g., reaction of $\text{PrCOCMe}_2\text{NH}_3^+ \text{Cl}^-$ with 2-amino-6-chloro-5-nitropyrimidin-4(3H)-one in refluxing EtOH contg. Et₃N for 24 h gave 55% pyrimidine I, which on treatment with NaOH and Na₂S₂O₄ in H₂O gave 91% pteridine II. Three routes to the amino ketones based on amino acids, NOCl addn. to alkenes, and nitro alcs. are discussed. These compds. are inhibitors of 6-hydroxymethyl-7,8-dihydropterin pyrophosphokinase, an enzyme in the path to dihydrofolate, and their inhibitory potencies are discussed in the light of a hypothetical active site model for the enzyme.

RX(19) OF 582



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REF: J. Chem. Soc., Perkin Trans. 1, (8), 1645-59; 1985

OF 7 CASREACT COPYRIGHT 2001 ACS

=> d ind 7

L59 ANSWER 7 OF 7 CASREACT COPYRIGHT 2001 ACS
 CC 28-17 (Heterocyclic Compounds (More Than One Hetero Atom))
 Section cross-reference(s): 7, 23
 ST pteridine prepn hydroxymethylpterin pyrophosphokinase inhibition; amino
 ketone prepn pteridine precursor
 IT Coupling reaction
 (of aminochloronitropyridinone with amino ketones, in prepn. of blocked
 dihydropteridines)
 IT Ketones, reactions
 RL: RCT (Reactant)
 (amino, coupling reactions of, with aminochloronitropyrimidinone, in
 prepn. of blocked dihydropteridines)
 IT Cyclocondensation reaction
 (intramol., of [(oxoalkyl)amino]nitroaminopyrimidinones, blocked
 dihydropteridines by)
 IT 96-22-0 108-94-1, reactions 2550-26-7
 RL: RCT (Reactant)
 (Wittig reaction of, with tri-Et phosphonoacetate)
 IT 867-13-0
 RL: RCT (Reactant)
 (Wittig reactions of, with ketones)
 IT 556-82-1 591-49-1 693-89-0 1191-16-8
 RL: RCT (Reactant)
 (addn. reaction of, with nitrosyl chloride)
 IT 2648-71-7
 RL: RCT (Reactant)
 (azidation of)
 IT 62-57-7
 RL: RCT (Reactant)
 (condensation reaction of, with phthalic anhydride)
 IT 85-44-9
 RL: RCT (Reactant)
 (condensation reactions of, with amino carboxylic acids)
 IT 36848-04-1 101232-03-5
 RL: RCT (Reactant)
 (coupling reaction of, with aminochloronitropyrimidinone)
 IT 64298-85-7
 RL: RCT (Reactant)
 (hydrolysis of)
 IT 50936-55-5
 RL: PROC (Process)
 (inhibition of, by blocked dihydropterins)
 IT 1194-21-4
 RL: RCT (Reactant)
 (nitration of)
 IT 20575-38-6
 RL: RCT (Reactant)
 (oxidn. and redn. of)
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 RL: RCT (Reactant)
 (oxidn. of)
 IT 14463-79-7P 101210-79-1P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and acid chloride formation of)
 IT 932-89-8P 39821-65-3P 55066-44-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and addn. reaction of, with nitrosyl chloride)
 IT 64282-11-7P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and amidation of, with phthalic anhydride)
 IT 4545-04-4P 88934-90-1P 101210-86-0P 101210-87-1P 101210-88-2P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and amination of)
 IT 32211-90-8P 101210-83-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and amine deprotection of)
 IT 13325-14-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and benzoylation of)
 IT 10201-10-2P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and catalytic hydrogenation of)

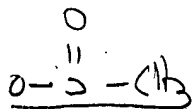
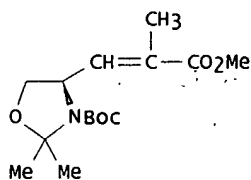
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Page 8

- IT 10201-16-8P 52312-36-4P 52312-37-5P 53931-60-5P 101210-85-9P
 101210-92-8P 101210-93-9P 101210-97-3P 101210-98-4P 101231-99-6P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and coupling reaction of, with aminochloronitropyrimidinone)
- IT 1007-99-4P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and coupling reactions of, with amino ketones, in prepn. of
 dihydropteridines)
- IT 32211-88-4P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and diazotization of)
- IT 86208-79-9P 101210-96-2P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and hydrogenation of)
- IT 32211-89-5P 37557-72-5P 101210-78-0P 101210-99-5P 101211-10-3P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and hydrolysis of)
- IT 10201-21-5P 37557-79-2P 52312-39-7P 52479-24-0P 53640-85-0P
 101211-01-2P 101211-06-7P 101211-14-7P 101211-15-8P 101224-20-8P
 101224-21-9P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and inhibition by, of hydroxymethyldihydropterin
 pyrophosphokinase)
- IT 10201-18-0P 37557-75-8P 52312-38-6P 52403-64-2P 101211-00-1P
 101211-02-3P 101211-04-5P 101211-05-6P 101211-07-8P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and intramol. cyclocondensation of, dihydropteridinone by)
- IT 101211-11-4P 101211-13-6P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and intramol. cyclocondensation reaction of, dihydropteridinone
 by)
- IT 37557-71-4P 101232-01-3P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and oxidn. of)
- IT 15249-93-1P 34188-63-1P 55591-26-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and redn. of)
- IT 10201-15-7P 13292-96-1P 32211-91-9P 101210-84-8P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. and semicarbazone formation of)
- IT 32211-92-0P 53640-81-6P 101210-82-6P 101210-89-3P 101210-91-7P
 101210-94-0P 101210-95-1P 101211-08-9P 101211-16-9P 101211-17-0P
 101232-00-2P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of)
- IT 101210-90-6P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., amination, and coupling reaction of, with
 aminochloronitropyrimidinone)
- IT 101210-81-5P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., chlorination, and hydrolysis of)
- IT 101210-80-4P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., diazotization, and chlorination of)
- IT 101232-02-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn., hydrolysis, and intramol. cyclocondensation of,
 dihydropteridinone by)
- IT 101211-03-4P 101211-09-0P 101211-12-5P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (prepn., oxidn., and inhibitory activity of, towards
 hydroxymethyldihydropterin pyrophosphokinase)

=> d bib abs

L35 ANSWER 1 OF 1 HCAPLUS COPYRIGHT 2001 ACS
 AN 1997:304675-HCAPLUS
 DN 127:17927
 TI Studies on 1,3-allylic strain control on dihydroxylations and hydrogenations of .alpha.-substituted enoates
 AU Kauppinen, Pasi M.; Koskinen, Ari M. P.
 CS Dep. Chem., Univ. Oulu, Oulu, FIN-90570, Finland
 SO Tetrahedron Lett. (1997), 38(17), 3103-3106
 CODEN: TELEAY; ISSN: 0040-4039
 PB Elsevier
 DT Journal
 LA English
 GI



I

AB L-Serine derived E- and Z-enoates I were subjected to catalytic dihydroxylation and hydrogenation reactions. The obsd. selectivities can be explained to arise from 1,3-allylic strain.

=> d ind

L35 ANSWER 1 OF 1 HCAPLUS COPYRIGHT 2001 ACS
 CC 34-2 (Amino Acids, Peptides, and Proteins)
 Section cross-reference(s): 28
 ST serine enoate deriv allylic strain control; allylic strain effect
 catalytic dihydroxylation hydrogenation
 IT Osmylation
 Stereoselective hydrogenation
 (studies on 1,3-allylic strain control on dihydroxylations and hydrogenations of .alpha.-substituted enoates)
 IT Unsaturated esters
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (.alpha.,.beta.-unsatd.; studies on 1,3-allylic strain control on dihydroxylations and hydrogenations of .alpha.-substituted enoates)
 IT 102308-32-7
 RL: RCT (Reactant)
 (studies on 1,3-allylic strain control on dihydroxylations and hydrogenations of .alpha.-substituted enoates)
 IT 190335-24-1P 190335-25-2P 190335-26-3P 190335-28-5P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
 (studies on 1,3-allylic strain control on dihydroxylations and hydrogenations of .alpha.-substituted enoates)
 IT 160412-90-8P 190335-27-4P 190335-29-6P 190335-30-9P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (studies on 1,3-allylic strain control on dihydroxylations and hydrogenations of .alpha.-substituted enoates)

L45 ANSWER 1 OF 11 CASREACT COPYRIGHT 2001 ACS

AN 131:271637 CASREACT

TI Carboxylic acid-2-acyloxymethyl-4-aminobutyl esters and hydrogenation method for producing them from the corresponding (un)saturated cyano esters

IN Schmidt, Beat; Stucky, Gerhard

PA Lonza A.-G., Switz.

SO PCT Int. Appl., 15 pp.

CODEN: PIXXD2

DT Patent

LA German

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
RI WO 9951566	A1	19991014	WO 1998-EP1955	19980402

W:	AL	AM	AT	AU	AZ	BA	BB	BG	BR	BY	CA	CH	CN	CU	CZ	DE
	DK	EE	ES	FI	GB	GE	GH	GM	GW	HU	ID	IL	IS	JP	KE	KG
	KP	KR	KZ	LC	LB	LR	LS	LT	LU	LV	MD	MG	MK	MN	MO	MX
	NO	NZ	PL	PT	RO	RU	SD	SE	SG	SI	SK	SL	TJ	TM	TR	TT
	UA	UG	US	UZ	VN	YU	ZW	AM	AZ	BY	KG	KZ	MD	RU	TJ	TM
RW:	GH	GM	KE	LS	MW	SD	SZ	UG	ZW	AT	BE	CH	CY	DE	DK	ES
	FI	FR	GB	GR	IE	IT	LU	MC	NL	PT	SE	BF	BJ	CF	CG	CI
	CM	GA	GN	ML	MR	NE	SN	TD	TG							

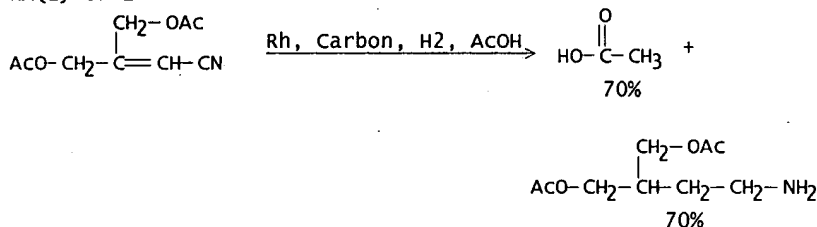
AU 9872141 A1 19991025 AU 1998-72141 19980402

PRAI WO 1998-EP1955 19980402

OS MARPAT 131:271637

AB Carboxylic acid-2-acyloxymethyl-4-aminobutyl esters
(R2OCH2)CH(CH2OR3)CH2CH2NHR1 (R1 = acid- or base-hydrolyzable
amino-blocking group; R2, R3 = C2-6 alkanoyl, benzoyl, salt), which are
intermediate products important for the introduction of the side-chain in
antiviral purine derivs. (no data), are prepd. in high yield and
selectivity by the hydrogenation of the corresponding (un)satd.
cyano esters. Thus, acetic acid-2-acetoxymethyl-3-cyanoallyl ester was
dissolved in AcOH and hydrogenated in the presence of 5% Rh/C at
10 bar for 2 h, producing 4-acetoxy-3-(acetoxymethyl)butylammonium acetate
in 70% yield.

RX(1) OF 1



REF: PCT Int. Appl., 9951566, 14 Oct 1999

OF 11 CASREACT COPYRIGHT 2001 ACS

RE.CNT 2

RE

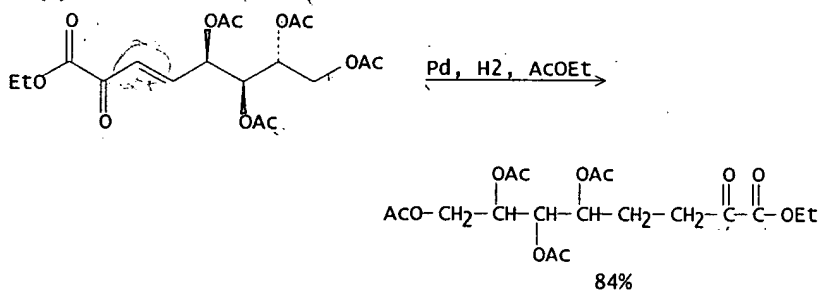
(1) Beecham Group Plc; EP 0369583 A 1990 CAPLUS

(2) Nishizawa, M; TETRAHEDRON LETTERS 1983, V24, P4447 CAPLUS

=> d bib abs fcrdref 2

L45 ANSWER 2 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 117:234402 CASREACT
 TI Enantiospecific syntheses of 3,4-dideoxyoct-2-ulosonic acids
 AU Shing, Tony K. M.
 CS Dep. Chem., Chin. Univ. Hong Kong, Shatin, Hong Kong
 SO Tetrahedron (1992), 48(33), 6777-86
 CODEN: TETRAB; ISSN: 0040-4020
 DT Journal
 LA English
 AB Et 5,6,7,8-tetra-O-acetyl-3,4-diideoxy-D-arabino-oct-2-ulosonate and Et 3,4-dideoxy-5,6;7,8-di-O-isopropylidene-D-arabino-oct-2-ulosonate have been synthesized from peracetylated and bisacetonated aldehydo-D-arabinose resp. by a two stage procedure: Wittig reaction and catalytic hydrogenation. Deprotection of the blocked Et oct-2-ulosonate afforded the 3,4-dideoxy-D-arabino-oct-2-ulosonic acid (4-deoxy-KDO), isolated as its calcium salt in an overall yield of 37% from D-arabinose. Likewise reactions of D-xylose gave calcium 3,4-dideoxy-D-xylo-oct-2-ulosonate in an overall yield of 34%. Both calcium salts were derivatized as cryst. quinoxaline tetraacetates. Other routes attempted are also described.

RX(2) OF 3

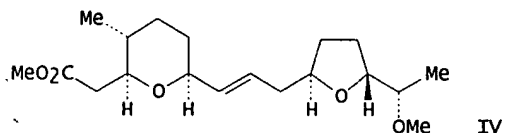
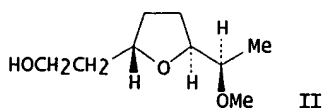
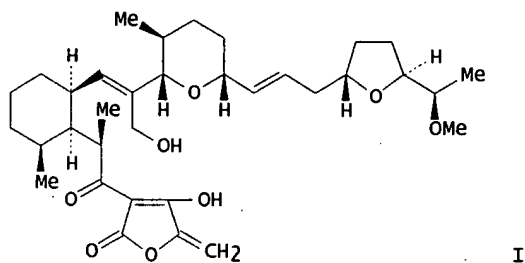


REF: Tetrahedron, 48(33), 6777-86; 1992

OF 11 CASREACT COPYRIGHT 2001 ACS

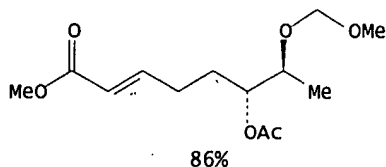
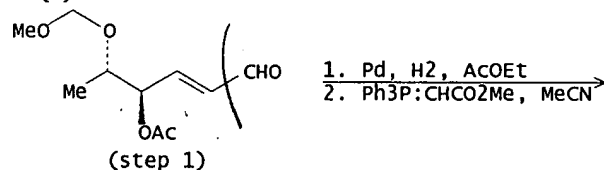
=> d bib abs fcdref 3

L45 ANSWER 3 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 112:76728 CASREACT
 TI Synthesis of the enantiomeric polyether fragment of tetronomycin
 AU Hori, Kozo; Nomura, Keiichi; Yoshii, Eiichi
 CS Fac. Pharm. Sci., Toyama Med. Pharm. Univ., Toyama, 930-01, Japan
 SO Heterocycles (1989), 29(4), 663-6
 CODEN: HTCYAM; ISSN: 0385-5414
 DT Journal
 LA English
 GI



AB The abs. stereochem. of tetronomycin (I), a novel acyltetronic acid ionophore, was confirmed by comparison of the degradn. product II with the synthetic enantiomer (III) derived from L-rhamnose. The enantiomer IV of the polyether subunit of I was synthesized by coupling III with the tetrahydropyran portion prep'd. from D-glucose.

RX(3) OF 122



REF: Heterocycles, 29(4), 663-6; 1989

OF 11 CASREACT COPYRIGHT 2001 ACS

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=> d bib abs fcdref 4

L45 ANSWER 4 OF 11 CASREACT COPYRIGHT 2001 ACS

AN 111:194341 CASREACT

TI Glycols in stereospecific synthesis. I. Synthesis of (+)-cis-disparlure, the sex pheromone of the gypsy moth (*Porthetria dispar* L)

AU Tolstikov, A. G.; Khakhalina, N. V.; Odinkov, V. N.; Khalilov, L. M.; Spirikhin, L. V.

CS Inst. Khim., Ufa, USSR

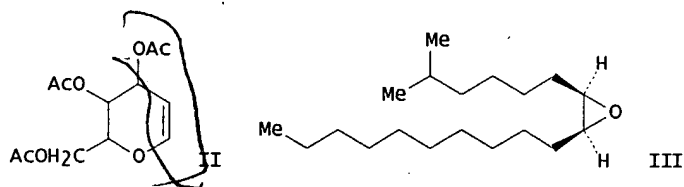
SO Zh. Org. Khim. (1989), 25(2), 296-302

CODEN: ZORKAE; ISSN: 0514-7492

DT Journal

LA Russian

GI



AB A novel route for the synthesis of 2R,3S-epoxy-1-tridecanol (I) starting from tri-O-acetyl-D-galactal (II) is described. Galactal II is useful as a synthon for (+)-cis-disparlure (III), the sex pheromone of the gypsy moth.

REYES 09/582,495

OF 11 CASREACT COPYRIGHT 2001 ACS

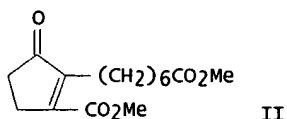
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SEARCHED BY SUSAN HANLEY 305-4053

Page 6

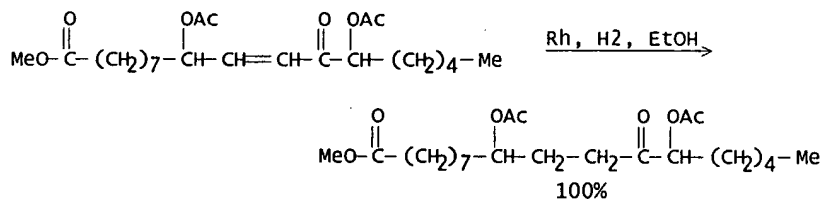
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L45 ANSWER 5 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 111:96897 CASREACT
 TI Castor oil to biologically active compounds. Part III. Ricinoleic acid to prostaglandins. I. Synthesis of methyl 2-[6-(methoxycarbonyl)hexyl]cyclopent-2-en-1-one-3-carboxylate and PGE1
 AU Swaminathan, Shankar; Singh, Vinod K.; Dev, Sukh
 CS Malti-Chem Res. Cent., Vadodara, 391 340, India
 SO Indian J. Chem., Sect. B (1988), 27B(12), 1069-75
 CODEN: IJSBDB; ISSN: 0376-4699
 DT Journal
 LA English
 GI



AB Ricinoleic acid was converted into Me 9,13-bisacetoxo-12-oxooctadecanoate (I), an envisaged key intermediate for the synthesis of prostanoids. As a preliminary, I was transformed into the title compd. (II) which was previously converted into PGE1.

RX(5) OF 78



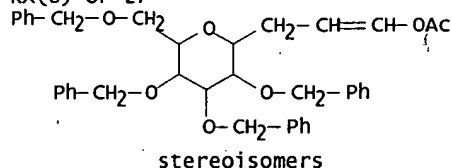
REF: Indian J. Chem., Sect. B, 27B(12), 1069-75; 1988

OF 11 CASREACT COPYRIGHT 2001 ACS

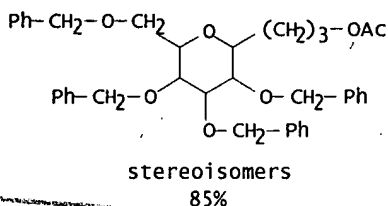
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L45 ANSWER 6 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 110:213215 CASREACT
 TI Oxygenated allylic silanes: useful homoenolate equivalents for the stereoselective C-glycosidation of pyranoside derivatives
 AU Panek, James S.; Sparks, Michelle A.
 CS Metcalf Cent. Sci. Eng., Boston Univ., Boston, MA, 02215, USA
 SO J. Org. Chem. (1989), 54(9), 2034-8
 CODEN: JOCEAH; ISSN: 0022-3263
 DT Journal
 LA English
 AB Acylated C1-oxygenated allylic silanes, 1-acetyloxy-2-propenyltrimethylsilane, 1-acetyloxy-2-methyl-2-propenyltrimethylsilane, and Et 2-propenyltrimethylsilane-1-carbonate function as homoenolate equivs. in C-glycosidation reactions of pyranoside derivs. The substituted allylic silanes participate in stereoelectronically controlled axial addns. to pyranoside oxonium ions produced through the action of BF₃.Et₂O on D-glucopyranoside and D-mannopyranoside derivs. The reactions resulted in the stereoselective C1-functionalization of the pyran ring with the incorporation of a 3-acetyloxy-2-propenyl, 3-acetyloxy-2-methyl-2-propenyl or an 3-ethoxycarbonyloxy-2-propenyl function. The facial selectivities of the reactions are good to excellent with .alpha.:.beta. ratios ranging from 5:1 to 10:1. The synthon equivalency for the reagents was established. The terminal enol esters of the C-glycosides were converted to their primary ester derivs. by catalytic hydrogenation or converted to their resp. carbonyl derivs. using a two-step oxidative cleavage sequence.

RX(8) OF 27



$\xrightarrow[\text{Pyridine}]{\text{Pd, H}_2, \text{MeOH}}$



REF: J. Org. Chem., 54(9), 2034-8; 1989

OF 11 CASREACT COPYRIGHT 2001 ACS

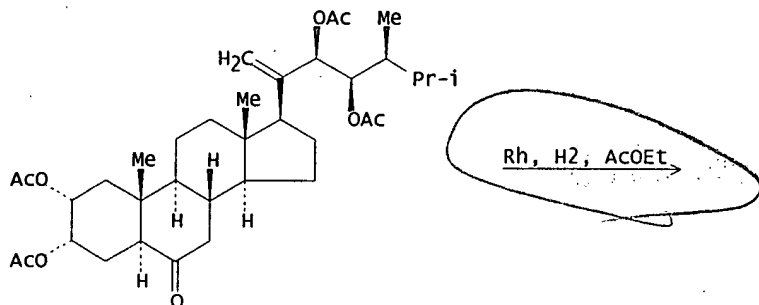
=> d bib abs fcrdref 7

L45 ANSWER 7 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 108:187052 CASREACT
 TI An improved synthesis of plant growth regulating steroid brassinolide and its congeners
 AU Kametani, Tetsuji; Katoh, Tadashi; Fujio, Junko; Nogiwa, Ikuno; Tsubuki, Masayoshi; Honda, Toshio
 CS Inst. Med. Chem., Hoshi Univ., Tokyo, 142, Japan
 SO J. Org. Chem. (1988), 53(9), 1982-91
 CODEN: JOCEAH; ISSN: 0022-3263
 DT Journal
 LA English
 GI

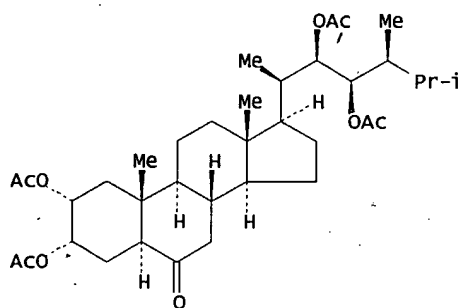
* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Brassinosteroids including brassinolide (I) and castasterone (II) were prepd. from pregnenolone (III).

RX(41) OF 45



RX(41) OF 45



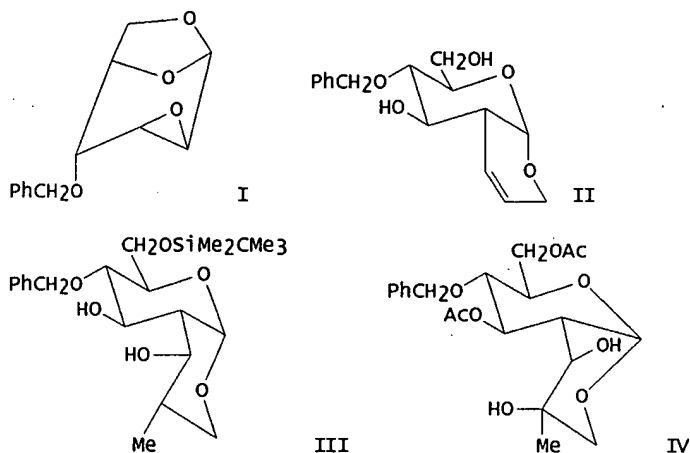
stereoisomers
47%

REF: J. Org. Chem., 53(9), 1982-91; 1988

OF 11, CASREACT—COPYRIGHT 2001 ACS

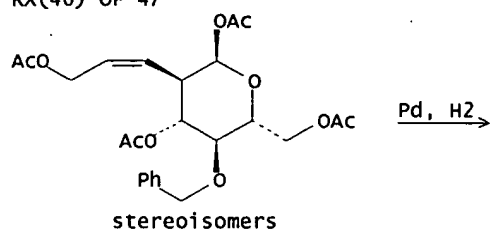
=> d bib abs fcrdref 8

L45 ANSWER 8 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 107:154621 CASREACT
 TI Dipyranoside precursors for ansamycins. Pyranosidic homologation. 5
 AU Fraser-Reid, Bert; Magdzinski, Leon; Molino, Bruce F.; Mootoo, David R.
 CS Paul M. Gross Chem. Lab., Duke Univ., Durham, NC, 27706, USA
 SO J. Org. Chem. (1987), 52(20), 4495-504
 CODEN: JOCEAH; ISSN: 0022-3263
 DT Journal
 LA English
 GI

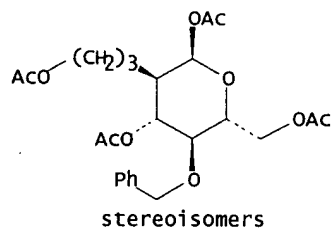


AB The process of pyranosidic homologation was applied to the readily obtainable dianhydro sugar I in the context of prepn. of precursors for mols. contg. multiple contiguous chiral centers (e.g., the ansa chains of rifamycin S and streptovaricin A). Two approaches for construction of the lower satellites were detd. The first involved opening of the epoxide I with a carbanion derived from propargyl alc., followed by Lindlar redn. Treatment of the resulting allylic alc. with CF₃CO₂H lead to internal glycosidation; the cis-fused (i.e., .alpha.) bicyclic system II being highly favored. II on sequential silylation, epoxidn., epoxide ring cleavage with LiMe₂C₄, pyridinium chlorochromate oxidn., and LiAlH₄ redn. gave III the precursor for rifamycin S. Also prepd. from I was IV, required for streptovaricin A.

RX(46) OF 47



$\xrightarrow{\text{Pd, H}_2}$

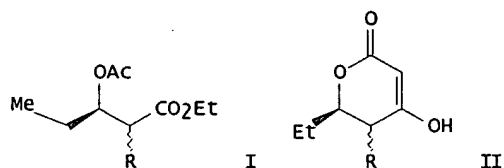


REF: J. Org. Chem., 52(20), 4495-504; 1987

OF 11 CASREACT COPYRIGHT 2001 ACS

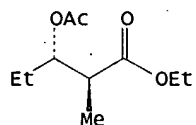
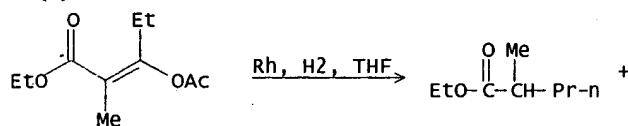
=> d bib abs fcrdref 9

L45 ANSWER 9 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 104:108994 CASREACT
 TI Studies on the intramolecular Claisen condensation. Stereospecific ring-closure of .beta.-acetoxy esters
 AU Brandaenge, Svante; Leijonmarck, Hans
 CS Dep. Org. Chem., Univ. Stockholm, Stockholm, S-106 91, Swed.
 SO J. Chem. Soc., Chem. Commun. (1985), (16), 1097-8
 CODEN: JCCCAT; ISSN: 0022-4936
 DT Journal
 LA English
 GI



AB The .beta.-acetoxy esters I (R = .alpha.-, .beta.-Me) underwent stereospecific ring closure on treatment with (Me₃Si)₂NLi in THF at -75.degree. under N for 1-2 h to give 59-65% dihydropyranone derivs. II (R as before).

RX(1) OF 14

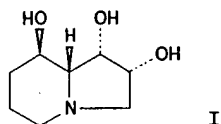


REF: J. Chem. Soc., Chem. Commun., (16), 1097-8; 1985

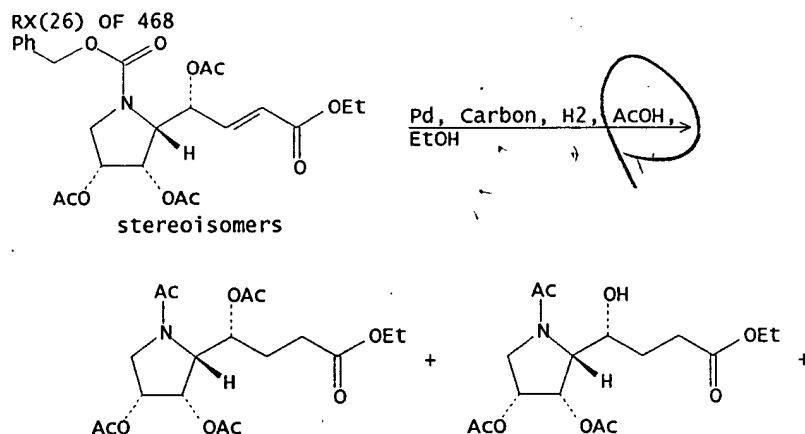
OF 11 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 10

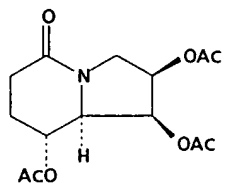
L45 ANSWER 10 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 103:142231 CASREACT
 TI Synthesis of the indolizidine alkaloid swainsonine from D-glucose
 AU Ali, Mezher H.; Hough, Leslie; Richardson, Anthony C.
 CS Dep. Chem., Queen Elizabeth Coll., London, W8 7AH, UK
 SO Carbohydr. Res. (1985), 136 225-40
 CODEN: CRBRAT; ISSN: 0008-6215
 DT Journal
 LA English
 GI



AB Since the stereochem. of the title alkaloid (I) exactly matches that of 3-amino-3-deoxy-D-mannose, the latter compd. is an ideal chiron for the synthesis of the former. Selective tosylation of Me 3-benzyloxycarbonylamino-3-deoxy-.alpha.-D-mannopyranoside, followed by removal of the benzyloxycarbonyl group and cyclization, afforded the 3,6-imine which was converted into its benzyloxycarbonyl deriv. Hydrolysis of the glycosidic group then afforded 3,6-benzyloxycarbonylimino-3,6-dideoxy-D-mannose. The attempted addn. of a C2 unit at C-1 by the Wittig or the Wadsworth-Emmons-Horner reaction either failed to give the required product or was followed by Michael addn. of 1 of the hydroxyl groups to the newly formed double-bond. 2,4,5-Tri-O-acetyl-3,6-benzyloxycarbonylimino-3,6-dideoxy-aldehyde-D-mannose was prepd. via the di-Et dithioacetal and condensed with ethoxycarbonylmethylenetriphenylphosphorane to give the Wittig adduct in good yield, which, on catalytic redn., underwent hydrogenation of the double bond, loss of the benzyloxycarbonyl group, and attack of the released amino group on either the terminal ethoxycarbonyl group or the 2-O-acetyl group to give a mixt. of the required cyclic lactam and the N-acetyl deriv. Redn. of the lactam with the borane-dimethyl sulfide complex afforded swainsonine triacetate, from which the parent alkaloid was obtained.



RX(26) OF 468

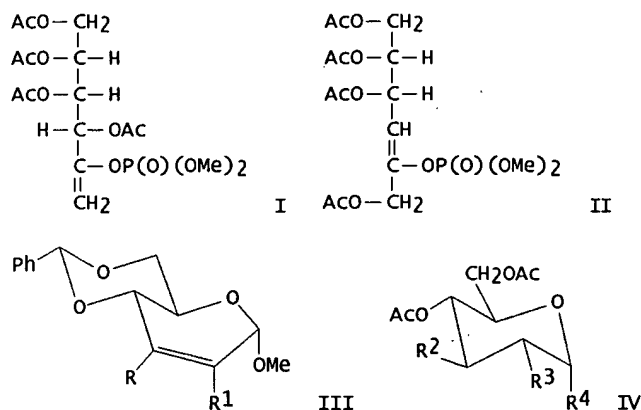


REF: Carbohydr. Res., 136, 225-40; 1985

OF 11 CASREACT COPYRIGHT 2001 ACS

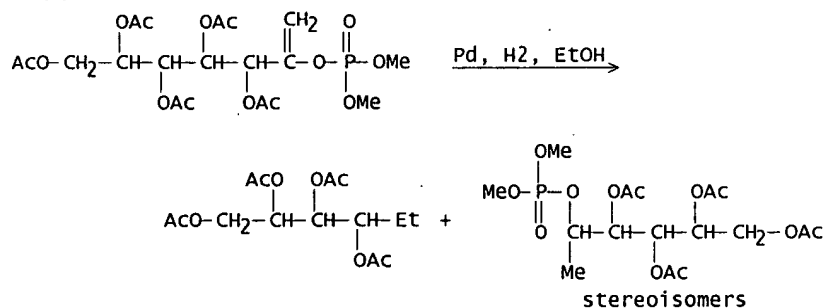
=> d bib abs fcdref 11

L45 ANSWER 11 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 103:22851 CASREACT
 TI Studies of hydrogenation of saccharide enol phosphates
 AU Thiem, Joachim; Rasch, Dieter
 CS Org.-Chem. Inst., Univ. Muenster, Muenster, D-4400, Fed. Rep. Ger.
 SO Liebigs Ann. Chem. (1985), (3), 536-44
 CODEN: LACHDL; ISSN: 0170-2041
 DT Journal
 LA German
 GI



AB Hydrogenation of the isomeric acyclic enol phosphates I and II in the presence of Pd/C gave predominantly epimeric deoxy phosphates. Similar hydrogenation of pyranoid enol phosphate III [R = H, R1 = OP(O)(OMe)2] followed by acetylation gave hexopyranoside IV [R2 = H, R3 = OP(O)(OMe)2, R4 = OMe], while III [R = OP(O)(OMe)2, R1 = H] gave anhydro product [IV; R2 = OP(O)(OMe)2, R3 = R4 = H]. Hydrogenation of Me 5-O-benzoyl-2-deoxy-3-O-(dimethoxyphosphoryl)-.beta.-D-glycero-pent-2-enofuranoside gave 1,4-anhydro-5-O-benzoyl-2,3-dideoxy-D-glycero-pentitol.

RX(1) OF 35



REF: Liebigs Ann. Chem., (3), 536-44; 1985

OF 11 CASREACT COPYRIGHT 2001 ACS

=> d bib abs hitstr 120 1

L20 ANSWER 1 OF 2 HCAPLUS* COPYRIGHT 2001 ACS

AN 1997:509106 HCAPLUS

DN 127:190471

TI Preparation of saturated esters from unsaturated esters

IN Tanaka, Yasutaka; Fukuya, Kazuaki

PA Daicel Chemical Industries, Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 09194427	A2	19970729	JP 1996-24686	19960118

OS CASREACT 127:190471; MARPAT 127:190471

AB Satd. esters are prepd. by hydrogenation of
R1R2C:CR3CR4R5O2CR6 (R1-R5 = C1-10 alkyl, H; R6 = C1-10 alkyl) by using
catalysts contg. 10-100 wt.% Ni. Allyl acetate and H were passed
through N111 (Ni catalyst supported on a carrier)-packed column
at 150.degree. over 8 h to give 92.8% Pr acetate.

IT 7440-02-0, Raney nickel, uses

RL: CAT (Catalyst use); USES (Uses)

(N 154; prepn. of satd. esters from unsatd. esters by using Ni
catalysts)

RN 7440-02-0 HCAPLUS

CN Nickel (8CI, 9CI) (CA INDEX NAME)

Ni

=> d bib abs hitstr 121 1

L21 ANSWER 1 OF 6 HCAPLUS /COPYRIGHT 2001 ACS
 AN 1999:565202 HCAPLUS
 DN 131:185786
 TI Unsaturated polyester-based thermosetting resin compositions for cured products with excellent transparency and heat and weather resistance
 IN Matsui, Fumio; Morita, Katsuhisa; Hatano, Yoshitaka; Shimizu, Akihiro
 PA Showa Highpolymer Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 6 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 11240923	A2	19990907	JP 1998-43795	19980225

AB The comps. with good handling and storage stability at an ambient temp. comprise (1) unsatd. polyesters prepd. from polyols (A), satd. polybasic acids (B), and unsatd. polybasic acids (A and/or B is alicyclic compds.), (2) diallyl phthalates, and (3) org. peroxides. Thus, 100 parts of an unsatd. polyester (Mn 3800, Mw 8200, softening temp. 71.3.degree.), which was prepd. from 1,4-cyclohexanedimethanol 144.5, 1,4-cyclohexanedicarboxylic acid 172.0, hydrogenated bisphenol A 243.8, adipic acid 29.2, and fumaric acid 92.8 g, was melt-kneaded with diallyl terephthalate 20, divinylbenzene 3, and dicumyl peroxide 2 parts, pelletized, and transfer-molded to give a test piece showing bending strength 7.5 kg/cm2, light transmittance 82%, glass-transition temp. 142.degree., and good heat resistance.

=> d ind

L21 ANSWER 1 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 IC ICM C08F283-01
 ICS C08K005-14; C08L067-06; C08G063-553; C08F283-01; C08F218-18
 CC 37-6 (Plastics Manufacture and Processing)
 ST alicyclic unsatd polyester heat resistance; cyclohexanedimethanol cyclohexanedicarboxylate fumarate unsatd polyester transparency; allyl terephthalate crosslink unsatd polyester
 IT Polyoxyalkylenes, preparation
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (polyester-, unsatd.; unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)
 IT Polyesters, preparation
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (polyoxyalkylene-, unsatd.; unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)
 IT Heat-resistant materials
 Transparent materials
 (unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)
 IT Polyesters, preparation
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (unsatd.; unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)
 IT 240427-42-3P, Adipic acid-1,4-cyclohexanedicarboxylic acid-1,4-cyclohexanedimethanol-diallyl terephthalate-divinylbenzene-fumaric acid-hydrogenated bisphenol A copolymer 240427-43-4P 240427-44-5P
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (unsatd. polyester-based thermosetting resin comps. with good transparency and heat and weather resistance)

=> d bib abs hitstr 121 2

L21 ANSWER 2 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1998:651099 HCAPLUS
 DN 129:303277
 TI Unsaturated polyester-thermoplastic resin compositions for cured articles
 with low thermal expansion and their use in composites with steel
 IN Matsui, Fumio; Morita, Katsuhisa; Nakajima, Hiroshi; Hoshino, Toshiaki
 PA Showa Highpolymer Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 8 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 10265662	A2	19981006	JP 1997-72142	19970325
AB	<p>The comps. comprise unsatd. polyesters, diallyl phthalates, thermoplastic resins having glass transition temp. (Tg) .ltoreq.150.degree., polymn. initiators, and inorg. fillers and their cured articles show cure shrinkage .ltoreq.0.1% and thermal expansion coeff. at room temp.-300.degree. 0.7 .times. 10-5-1.5 .times. 10-5/.degree.C. The composites consisting of the polymer comps. and steel are also claimed. Thus, a mixt. contg. 1,4-butanediol-dimethyl terephthalate-fumaric acid copolymer, diallyl terephthalate, polystyrene, styrene monomer, dicumyl peroxide, SiO2 powders, and microcapsulated red P was press-molded and cured to give a test piece showing cure shrinkage 0.05%, Tg 308.degree., linear thermal expansion coeff. at 100.degree. 0.9 .times. 10-5/.degree.C, and flammability rating V-0.</p>				

=> d bib abs hitstr 121 3

L21 ANSWER 3 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1993:541378 HCAPLUS
 DN 119:141378
 TI Unsaturated polyester compositions and their use as binders in putty
 IN Fujishima, Minoru
 PA Hitachi Chemical Co Ltd, Japan
 SO Jpn. Kokai Tokkyo Koho, 7 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 05078459	A2	19930330	JP 1991-240105	19910920
AB	Title compns., applicable to zinc-treated anticorrosive steel sheets to form heat shock- and moisture-resistant films with good adhesion and polishing quality and useful for automobile repair, comprise 30-80% unsatd. polyesters obtained from polybasic acids contg. 0-90 mol% satd. acids and 10-100 mol% .alpha.,.beta.-unsatd. acids and polyhydric alcs. contg. 20-60 mol% hydrogenated bisphenol A and 10-40 mol% allyl glycidyl ether at alcs./acids = 1.0-2.0 (mol) and 20-70% liq. polymerizable compds. Thus, a mixt. of Rikabinol HB 813.6, diethylene glycol 239.7, maleic anhydride 553.7, and hydroquinone 0.2 part was heated in xylene, then heated with 193.2 parts Epiol A in the presence of Cation M2-100 (dimethyldodecylbenzylammonium chloride) to give an unsatd. polyester, which was dild. with styrene contg. hydroquinone. A putty contg. the unsatd. polyester compns., diethylaniline, Co naphthenates, .alpha.-naphthoquinone (stabilizer), TiO2, and talc was mixed with MEK peroxide, applied to a galvanized iron sheet at 2-mm thickness, and dried at 20.degree. for 14 min to form a film, which was polishable after 4 h and showed good adhesion and resistance to moisture and 4 heat cycles (80.degree./2 h .dblarw. -20.degree./2 h).				

=> d bib abs hitstr 121 4

L21 ANSWER 4 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1992:7470 HCAPLUS
 DN 116:7470
 TI Unsaturated polyester molding materials with high flash point and low shrinkage
 IN Kubo, Toshio; Sawano, Shin
 PA Matsushita Electric Works, Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 4 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 03192108	A2	19910822	JP 1989-331538	19891221
AB	The title materials comprise unsatd. polyesters, diallyl phthalate (I), thermoplastic resins, and styrene. Thus, with 80 parts 70:30 mixt. of hydrogenated bisphenol-based unsatd. polyester and I was blended a 30:70 polystyrene-styrene mixt. 20, BPO 1, Zn stearate 7, CaCO ₃ 300, and glass fibers 75 parts and then hot pressed at 100 kg/cm ² and 160.degree. for 90 s to give a molding with flash point 59.degree. and shrinkage 0.31%, vs. .gtoreq.100 and 0.38, resp., for a control without polystyrene-styrene mixt.				

=> d bib abs hitstr 121 5

L21 ANSWER 5 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1991:145647 HCAPLUS
 DN 114:145647
 TI Radiation-curable resin compositions containing modified cyclopentadiene
 polymers as binders for inks and coatings
 IN Suzuki, Akinori; Sasaki, Makoto; Tsucha, Shozo
 PA Nippon Oil Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 9 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 02215805	A2	19900828	JP 1989-36356	19890217
GI					



Rn I

AB The title compns. contain 10-95 parts diluents and 5-90 parts curable resins prepd. by thermal polymn. of 100 parts cyclopentadienes I (R = C1-3 alkyl; n = 0-6) and/or their Diels-Alder adducts with 0-50 parts arom. olefins and 2-120 parts pentaerythritol di- or triallyl ether or trimethylolpropane diallyl ether and esterifying the resulting OH-contg. resins and/or their hydrogenated derivs. with .alpha.,.beta.-unsatd. carboxylic acids at acid/OH equiv ratio 0.1-1.1 after optional treatment of part of OH with polyisocyanates, polycarboxylic acids, or their esters. Thus, polymg. dicyclopentadiene 700, pentaerythritol allyl ether 210, and pentaerythritol diallyl ether 90 g in xylene at 260.degree. for 3 h and esterifying 100 g of the resulting resin (OH value 0.135 mol/100 g) with 10.7 g acrylic acid in benzene-MIBK mixt. in presence of p-Mec6H4SO3H and hydroquinone at 100.degree. for 14 h gave a resin. An ink contg. the resin 32, trimethylolpropane triacrylate 44, Carmine 6B 17, Irgacure 184 7, and hydroquinone 0.1 part showed UV curing time 3 s, good gloss, and excellent misting resistance.

=> d bib abs hitstr 121 6

L21 ANSWER 6 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1975:141718 HCAPLUS
 DN 82:141718
 TI Unsaturated polyester compositions
 IN Miyawaki, Takeshi; Yutani, Seisuke; Takahama, Yoshio; Nikki, Masao
 PA Japan Catalytic Chemical Industry Co., Ltd.
 SO Japan. Kokai, 8 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 49130989	A2	19741216	JP 1973-44062	19730420
	JP 52039634	B4	19771006		
AB	Unsatd. polyesters (20-80 parts) were mixed with 20-80 parts crosslinking agents [65-99 wt.% styrene (I) [100-42-5], chlorostyrene, and(or) vinyltoluene and 1-35 wt.% diallyl phthalate (II) [131-17-9], diallyl isophthalate, triallyl cyanurate, triallyl isocyanurate, and(or) acrylates or methacrylates (b. >200.degree.)) and hardened to give smooth coatings with improved luster. Thus, maleic anhydride 980, trimethylolpropane diallyl ether 449, ethylene glycol 586, and a partially esterified product of a 1:1 hydrogenated rosin-trimethylolpropane mixt. 456 parts were polymd. at 180.degree. in N; a mixt. of the unsatd. polyester (acid no. 17)(100 parts), 10 parts II, and 100 parts I was mixed with 1 wt.% cumene hydroperoxide and 0.5 wt.% Co octenate, spray-coated (300.mu. thickness) on a laminated panel, and hardened 7 min at 80.degree. to give a pinhole-free coating.				

=> d bib abs 113 1

L13 ANSWER 1 OF 6 HCAPLUS ' COPYRIGHT 2001 ACS
 AN 2000:772590 HCAPLUS
 DN 133:336867
 TI Manufacture of hydrogenated esters,
 hydrogenation catalysts for use therein, and preparation
 of catalysts
 IN Ohga, Kazuhiko; Fujimoto, Masayuki; Uchida, Hiroshi; Tajima, Tsuneo
 PA Showa Denko K. K., Japan
 SO PCT Int. Appl., 78 pp.
 CODEN: PIXXD2
 DT Patent
 LA Japanese
 FAN.CNT 1

PATENT NO. KIND DATE APPLICATION NO. DATE

PI WO 2000064852 AI 20001102 WO 2000-JP977 20000221

W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU,
 CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL,
 IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
 MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
 SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ,
 BY, KG, KZ, MD, RU, TJ, TM
 RW: GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE,
 DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF,
 CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

PRAI JP 1999-118874 19990427
 US 1999-141247 19990630
 JP 1999-193352 19990707
 US 1999-147812 19990810
 JP 1999-284520 19991005
 US 1999-162896 19991101

OS MARPAT 133:336867

AB A process for highly selectively obtaining a hydrogenated
 ester from an unsatd. ester comprises
 hydrogenating the unsatd. ester in an inert solvent
 using a catalyst contg. at least one metal selected among the
 elements in Groups 8, 9, and 10 of the Periodic Table.

RE.CNT 4
 RE
 (1) Daicel Chemical Industries Ltd; JP 09194427 A 1997 HCAPLUS
 (2) Mitsubishi Gas Chemical Company Inc; JP 10120605 A 1998 HCAPLUS
 (3) Tosoh Corporation; JP 06279012 A 1994 HCAPLUS
 (4) Ube Industries Ltd; JP 1147597 A 1999

IDS

=> d bib abs 131 1

L31 ANSWER 1 OF 4 HCAPLUS COPYRIGHT 2001 ACS
 AN 2001:217747 HCAPLUS
 TI Raney metal fixed bed catalyst for
 hydrogenation of saturated and unsaturated
 esters and the manufacture and use thereof
 IN Ostgard, Daniel; Berweiler, Monika; Bender, Barbara; Stein, Gernot;
 Moebus, Konrad
 PA Degussa-Huls A.-G., Germany
 SO Jpn. Kokai Tokkyo Koho, 9 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001079410	A2	20010327	JP 2000-229531	20000728
	DE 19936135	A1	20010215	DE 1999-19936135	19990731
PRAI	DE 1999-19936135		19990731		
	US 1999-368571		19990805		

AB The invention relates to the Raney metal fixed bed catalyst from a Raney process metal, a catalyst promoter, a binder, and a wetting agent, wherein the catalyst molded to a certain shape is roasted at 100 to 850 degrees, activated by an alk. soln., and dipping it in a soln. contg. perrhenic acid and Rh salts for doping of the catalyst. The catalyst is able to carry out the hydrogenation of maleic acid for the formation of gamma-butyrolactone, THF, and 1,4-butanediol at 200 degrees and 80 bar, and has a higher selectivity than a Cu chromite catalyst.

=> d ind

L31 ANSWER 1 OF 4 HCAPLUS COPYRIGHT 2001 ACS
 IC ICM B01J025-02
 ICS C07C029-149; C07C031-125; C07C031-20; C07D307-08; C07D307-33;
 C07B061-00
 CC 67-1 (Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms)
 Section cross-reference(s): 22
 ST Raney metal fixed bed catalyst rhenium doping
 IT Hydrogenation
 Hydrogenation catalysts
 (Raney metal fixed bed catalyst for
 hydrogenation of satd. and unsatd. esters)
 IT 7440-02-00, Nickel, doped with rhenium
 RL: CAT (Catalyst use); PEP (Physical, engineering or chemical process);
 PROC (Process); USES (Uses)
 (Raney metal fixed bed catalyst for
 hydrogenation of satd. and unsatd. esters)
 IT 110-30-5P
 RL: PNU (Preparation, unclassified); PREP (Preparation)
 (Raney metal fixed bed catalyst for
 hydrogenation of satd. and unsatd. esters)
 IT 110-16-7, Maleic acid
 RL: RCT (Reactant)
 (Raney metal fixed bed catalyst for
 hydrogenation of satd. and unsatd. esters)
 IT 96-48-0P, gamma-Butyrolactone 109-99-9P, THF 110-63-4P,
 1,4-Butanediol
 RL: PNU (Preparation, unclassified); PREP (Preparation)
 (formation by Raney metal fixed bed catalyst)
 IT 7440-15-5, Rhenium 13768-11-1, Perrhenic acid
 RL: MOA (Modifier or additive use); USES (Uses)
 (prepn. of Raney metal fixed bed catalyst for
 hydrogenation of satd. and unsatd. esters)

- unsatd. fatty acid esters in fixed
beds of molded catalysts of metal powders)
- IT 7439-89-6, Iron, uses 7440-02-0, Nickel, uses 11102-42-4 51602-58-5
178415-17-3 178415-18-4 178415-19-5 178415-20-8
RL: CAT (Catalyst use); USES (Uses)
(continuous hydrogenation of unsatd. fatty acid
esters in fixed beds of molded catalysts of
metal powders)
- IT 112-61-8p, Methyl stearate
RL: IMF (Industrial manufacture); PREP (Preparation)
(continuous hydrogenation of unsatd. fatty acid
esters in fixed beds of molded catalysts of
metal powders)
- IT 112-63-0, Methyl linoleate
RL: RCT (Reactant)
(continuous hydrogenation of unsatd. fatty acid
esters in fixed beds of molded catalysts of
metal powders)

=> d bib abs 131 4

L31 ANSWER 4 OF 4 HCAPLUS COPYRIGHT 2001 ACS
 AN 1982:181787 HCAPLUS
 DN 96:181787
 TI Unsaturated acids and esters
 IN Shaw, Wilfrid G.; Rinz, James E.; Paparizos, Christos
 PA Standard Oil Co., USA
 SO U.S., 4 pp.
 CODEN: USXXAM
 DT Patent
 LA English
 FAN.CNT 1

PATENT-NO.	KIND	DATE	APPLICATION NO.	DATE
US 4307247	A	19811222	US 1980-184591	19800905
CA 1150732	A1	19830726	CA 1981-378937	19810603
JP 57050939	A2	19820325	JP 1981-112911	19810717
EP 47578	A1	19820317	EP 1981-303409	19810724
EP 47578	B1	19840530		

R: BE, CH, DE, FR, GB, IT, LU, NL, SE
 PRAI US 1980-184591 19800905

AB Satd., lower aliph. acids and esters are oxydehydrogenated to the corresponding unsatd. acids and esters using a catalyst of the formula $M_1M_2P_0.1-3Bi_0.01-2M_0.1-3Cu_0.01-2V_0.01-3M_1aM_2bOc$, where $M = K, Rb, Cs$; $M_1 = Ba, Cd, Ga, Ti, Zn$; $M_2 = Ca, Ce, Co, Cr, Fe, Mg, Ni, Ta, Tl$; $a = 0-2$; $b = 0-2$; and $c = no. to satisfy valence requirements of elements present$. Thus, $RbOH$ and $Ba(OH)_2$ were added to an aq. soln. of $(NH_4)_6Mo_7O_{24}$ at 30-35.degree.. After 15 min Cu acetate and NH_4VO_3 solns. were added, followed by a $BiCl_3-HCl$ soln. The slurry was heated 2 h at .apprx.70.degree., mixed with H_3PO_4 , and stirred for 30 min. The pH was then adjusted to 5.6, and the mixt. dried to give a powder catalyst precursor ($M_1M_2PRbBa_0.2Bi_0.25Cu_0.25V_0.25Oc$), which was coated on Al_2O_3 spheres. After calcing at 326-370.degree. for 3 h in a downward-flow, fixed-bed reactor, air, water, and isobutyric acid (I) [79-31-2] (I-catalyst vol. ratio 51.6, air-I mol. ratio 4.6, and H_2O -I ratio 25.3) were fed into the reactor to give methacrylic acid [79-41-4] in 61.3% yield (91.1% I inversion).

=> d bib abs hitstr 1

L73 ANSWER 1 OF 9 HCAPLUS COPYRIGHT 2001 ACS

AN 1998:498375 HCAPLUS

DN 129:175360

TI Regeneration of palladium catalysts for hydrogenation of diacetoxybutene into diacetoxybutane

IN Murai, Nobuyuki; Iwasaka, Hiroshi; Nishimura, Seiji

PA Mitsubishi Chemical Industries Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 10202106	A2	19980804	JP 1997-5981	19970117

AB The title catalysts comprising Pd supported on activated C, are regenerated by treating with steam and/or hot water. A mixt. contg. 84.5 wt.% 1,4-diacetoxybutene (I) and 9.5 wt.% 3,4-diacetoxybutene (II) was hydrogenated over Pd/activated-C by continuously feeding into a reactor at 50 g/h, resulting in residual I and II contents of 0.4 and 0.01 wt.%, resp., 4 h later and 2.5 and 0.2 wt.%, resp., 8000 h later. Then, the catalyst with lowered activity, was regenerated by treating with steam at 100.degree. for 7 h to recover its initial activity.

IT 7440-05-3, Palladium, uses

RL: CAT (Catalyst use); PEP (Physical, engineering or chemical process);

PROC (Process); USES (Uses)

(steam or hot water in regeneration of Pd/activated-C catalysts for hydrogenation of diacetoxybutene into diacetoxybutane)

RN 7440-05-3 HCAPLUS

CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 18085-02-4P, 3,4-Diacetoxy-1-butene

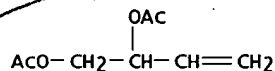
RL: RCT (Reactant); SPN (Synthetic preparation); PREP

(Preparation)

(steam or hot water in regeneration of Pd/activated-C catalysts for hydrogenation of diacetoxybutene into diacetoxybutane)

RN 18085-02-4 HCAPLUS

CN 3-Butene-1,2-diol, diacetate (8CI, 9CI) (CA INDEX NAME)



str 3

OF 9 HCAPLUS COPYRIGHT 2001 ACS

3655 HCAPLUS

563

ure for production of butanediol by the catalytic acetoxylation of
ene followed by hydrogenation and hydrolysis

, Nobuyuki; Iwasaka, Hiroshi

ubishi Chemical Corp., Japan

. Offen., 8 pp.

EN: GWXXBX

L Patent

L German

FA INT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 19741729	A1	19980326	DE 1997-19741729	19970922
	CA 2215544	AA	19980324	CA 1997-2215544	19970915
	JP 10152450	A2	19980609	JP 1997-250287	19970916
PRAI	JP 1996-251455		19960924		

AB Butanediol (i.e., 1,4-butanediol), useful as a monomer and chem. intermediate, is prepd. in high yield and selectivity by the catalytic acetoxylation of butadiene with ACOH in the presence of a Pd catalyst, hydrogenation of the diacetoxybutene intermediate to diacetoxybutane, and hydrolysis of the diacetoxybutane which contains .ltoreq.0.5% diacetoxyoctane. A process flow diagram is presented.

IT 7440-05-3, Palladium, uses
RL: CAT (Catalyst use); USES (Uses)
(procedure for prodn. of 1,4-butanediol by the catalytic acetoxylation of butadiene followed by hydrogenation and hydrolysis)

RN 7440-05-3 HCAPLUS

CN Palladium (8CI, 9CI) (CA INDEX NAME)

Pd

IT 18085-02-4P, Diacetoxybutene
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
(procedure for prodn. of 1,4-butanediol by the catalytic acetoxylation of butadiene followed by hydrogenation and hydrolysis)

RN 18085-02-4 HCAPLUS

CN 3-Butene-1,2-diol, diacetate (8CI, 9CI) (CA INDEX NAME)

OAC

ACO-CH₂-CH-CH=CH₂

=> d bib abs hitstr 4

L73 ANSWER 4 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1992:489825 HCAPLUS
 DN 117:89825
 TI Selective hydrogenation of olefins
 IN Chalk, Alan J.; Wertheimer, Laszlo V.
 PA Givaudan Corp., USA
 SO U.S., 10 pp.
 CODEN: USXXAM
 DT Patent
 LA English
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5118837	A	19920602	US 1987-13608	19870212
OS	CASREACT 117:89825; MARPAT 117:89825				
AB	Olefins contg. more than 1 double bond were selectively hydrogenated in the presence of a catalyst system consisting of a heterogeneous Ru catalyst, water, and a modifier. The hydrogenation is carried out at 0-100.degree. and pressures up to 2000 psig. Thus, 8.4 g 1-acetoxyocta-2,7-diene (I) was hydrogenated for 1.5 h in a mixt. of 3 mL H ₂ O, 0.12 g Ru/C, 1.15 mmol P(OBu) ₃ as a modifier and 15 mL EtOH at 25.degree. and 50 psi to give 98.9% conversion of I with 98.4 selectivity for 1-acetoxyoct-2-ene, which was present in 97.3% purity.				
IT	2371-13-3P, 1-Acetoxyoct-2-ene RL: SPN (Synthetic preparation); PREP (Preparation) (prepn. of, by selective hydrogenation of diene)				
RN	2371-13-3 HCAPLUS				
CN	2-Octen-1-ol, acetate (7CI, 8CI, 9CI) (CA INDEX NAME)				

$$\text{ACO}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{Me}$$

IT 7440-16-6, Rhodium, uses 7440-18-8, Ruthenium, uses
 RL: USES (Uses)
 (selective hydrogenation catalysts, for dienes)
 RN 7440-16-6 HCAPLUS
 CN Rhodium (8CI, 9CI) (CA INDEX NAME)

Rh

RN 7440-18-8 HCAPLUS
 CN Ruthenium (8CI, 9CI) (CA INDEX NAME)

Ru

IT 3491-26-7, 3-Acetoxyocta-1,7-diene 3491-27-8,
 1-Acetoxyocta-2,7-diene
 RL: RCT (Reactant)
 (selective hydrogenation of)
 RN 3491-26-7 HCAPLUS
 CN 1,7-Octadien-3-ol, acetate (7CI, 8CI, 9CI) (CA INDEX NAME)

$$\begin{array}{c} \text{OAC} \\ | \\ \text{H}_2\text{C}=\text{CH}-\text{CH}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2 \end{array}$$

RN 3491-27-8 HCAPLUS
 CN 2,7-Octadien-1-ol, acetate (7CI, 8CI, 9CI) (CA INDEX NAME)

$$\text{ACO}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2$$

=> d bib abs hitstr 9

L73 ANSWER 9 OF 9 HCAPLUS COPYRIGHT 2001 ACS

AN 1977:29609 HCAPLUS

DN 86:29609

TI Tetrahydrofuran

IN Smith, William Edward

PA General Electric Co., USA

SO Ger. Offen., 15 pp.

CODEN: GWXXBX

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 2461769	A1	19760701	DE 1974-2461769	19741228
AB	THF was prepd. cheaply and quant. by dehydroacetoxylation of $\text{AcO}(\text{CH}_2)_4\text{OH}$. Thus, propylene, AcOH , O_2 , and H_2O was passed through 0.3% Pd and 3% KOAc on Al_2O_3 at 180.degree., the product $\text{CH}_2\text{:CHCH}_2\text{OAc}$ hydroformylated-hydrogenated with $\text{H}_2\text{-CO}$ and $\text{Co}(\text{CO})_8$, the resultant $\text{AcO}(\text{CH}_2)_3\text{CHO}$ hydrogenated, and the $\text{AcO}(\text{CH}_2)_4\text{OH}$ so obtained cyclized to give 64% THF (based on $\text{CH}_2\text{:CHCH}_2\text{OAc}$).				
IT	7440-05-3, uses and miscellaneous RL: USES (Uses) (potassium acetate and, acetoxylation of propylene in presence of)				
RN	7440-05-3 HCAPLUS				
CN	Palladium (8CI, 9CI) (CA INDEX NAME)				

Pd

IT 591-87-7P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)

(prepn. and hydroformylation-hydrogenation of)

RN 591-87-7 HCAPLUS

CN Acetic acid, 2-propenyl ester (9CI) (CA INDEX NAME)

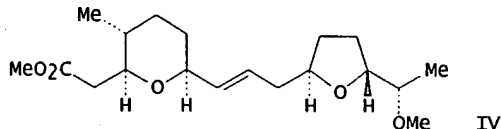
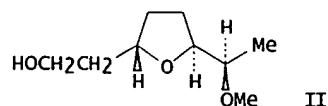
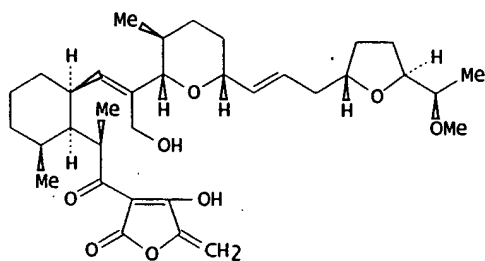
 $\text{AcO-CH}_2\text{-CH=CH}_2$

99 51566

Page 1

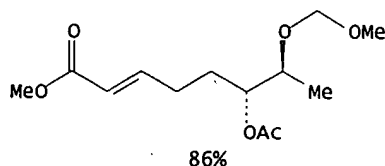
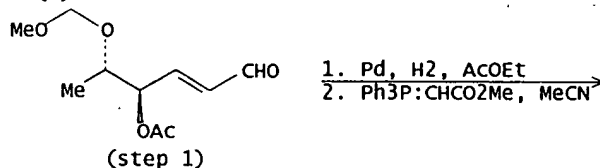
=> d bib abs fcrdref 3

L45 ANSWER 3 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 112:76728 CASREACT
 TI Synthesis of the enantiomeric polyether fragment of tetronomycin
 AU Hori, Kozo; Nomura, Keiichi; Yoshii, Eiichi
 CS Fac. Pharm. Sci., Toyama Med. Pharm. Univ., Toyama, 930-01, Japan
 SO Heterocycles (1989), 29(4), 663-6
 CODEN: HTCYAM; ISSN: 0385-5414
 DT Journal
 LA English
 GI



AB The abs. stereochem. of tetronomycin (I), a novel acyltetronic acid ionophore, was confirmed by comparison of the degradn. product II with the synthetic enantiomer (III) derived from L-rhamnose. The enantiomer IV of the polyether subunit of I was synthesized by coupling III with the tetrahydropyran portion prepd. from D-glucose.

RX(3) OF 122



REF: Heterocycles, 29(4), 663-6; 1989

OF 11 CASREACT COPYRIGHT 2001 ACS

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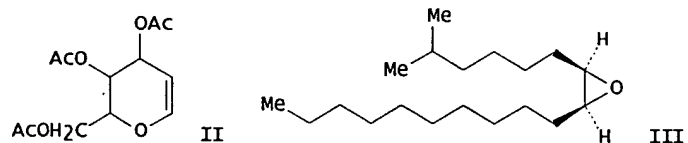
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=> d bib abs fcrdref 4

L45 ANSWER 4 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 111:194341 CASREACT
 TI Glycols in stereospecific synthesis. I. Synthesis of (+)-cis-disparlure,
 the sex pheromone of the gypsy moth (*Porthetria dispar* L)
 AU Tolstikov, A. G.; Khakhalina, N. V.; Odinokov, V. N.; Khalilov, L. M.;
 Spirikhin, L. V.
 CS Inst. Khim., Ufa, USSR
 SO Zh. Org. Khim. (1989), 25(2), 296-302
 CODEN: ZORKAE; ISSN: 0514-7492
 DT Journal
 LA Russian
 GI



AB A novel route for the synthesis of 2R,3S-epoxy-1-tridecanol (I) starting from tri-O-acetyl-D-galactal (II) is described. Galactal II is useful as a synthon for (+)-cis-disparlure (III), the sex pheromone of the gypsy moth.

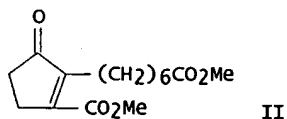
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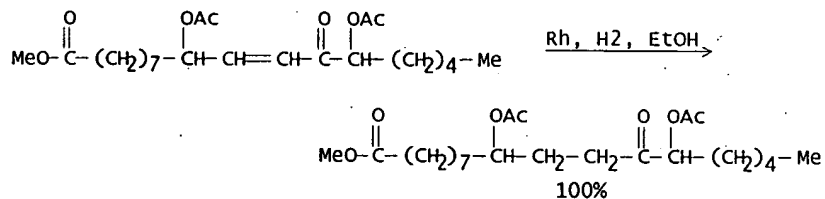
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L45 ANSWER 5 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 111:96897 CASREACT
 TI Castor oil to biologically active compounds. Part III. Ricinoleic acid to prostaglandins. I. Synthesis of methyl 2-[6-(methoxycarbonyl)hexyl]cyclopent-2-en-1-one-3-carboxylate and PGE1
 AU Swaminathan, Shankar; Singh, Vinod K.; Dev, Sukh
 CS Malti-Chem Res. Cent., Vadodara, 391 340, India
 SO Indian J. Chem., Sect. B (1988), 27B(12), 1069-75
 CODEN: IJSBDB; ISSN: 0376-4699
 DT Journal
 LA English
 GI



AB Ricinoleic acid was converted into Me 9,13-bisacetoxo-12-oxooctadecanoate (I), an envisaged key intermediate for the synthesis of prostanoids. As a preliminary, I was transformed into the title compd. (II) which was previously converted into PGE1.

RX(5) OF 78



REF: Indian J. Chem., Sect. B, 27B(12), 1069-75; 1988

QF 11 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 6

L45 ANSWER 6 OF 11 CASREACT COPYRIGHT 2001 ACS

AN 110:213215 CASREACT

TI Oxygenated allylic silanes: useful homoenolate equivalents for the stereoselective C-glycosidation of pyranoside derivatives

AU Panek, James S.; Sparks, Michelle A.

CS Metcalf Cent. Sci. Eng., Boston Univ., Boston, MA, 02215, USA

SO J. Org. Chem. (1989), 54(9), 2034-8

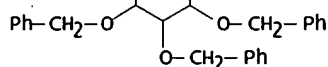
CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

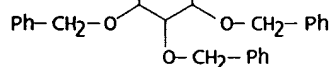
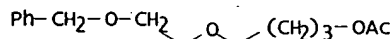
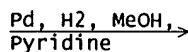
LA English

AB Acylated C1-oxygenated allylic silanes, 1-acetyloxy-2-propenyltrimethylsilane, 1-acetyloxy-2-methyl-2-propenyltrimethylsilane, and Et 2-propenyltrimethylsilane-1-carbonate function as homoenolate equivs. in C-glycosidation reactions of pyranoside derivs. The substituted allylic silanes participate in stereoelectronically controlled axial addns. to pyranoside oxonium ions produced through the action of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ on D-glucopyranoside and D-mannopyranoside derivs. The reactions resulted in the stereoselective C1-functionalization of the pyran ring with the incorporation of a 3-acetyloxy-2-propenyl, 3-acetyloxy-2-methyl-2-propenyl or an 3-ethoxycarbonyloxy-2-propenyl function. The facial selectivities of the reactions are good to excellent with α .. β . ratios ranging from 5:1 to 10:1. The synthon equivalency for the reagents was established. The terminal enol esters of the C-glycosides were converted to their primary ester derivs. by catalytic hydrogenation or converted to their resp. carbonyl derivs. using a two-step oxidative cleavage sequence.

RX(8) OF 27

$$\text{Ph}-\text{CH}_2-\text{O}-\text{CH}_2$$


stereoisomers



stereoisomers

85%

REF: J. Org. Chem., 54(9), 2034-8; 1989

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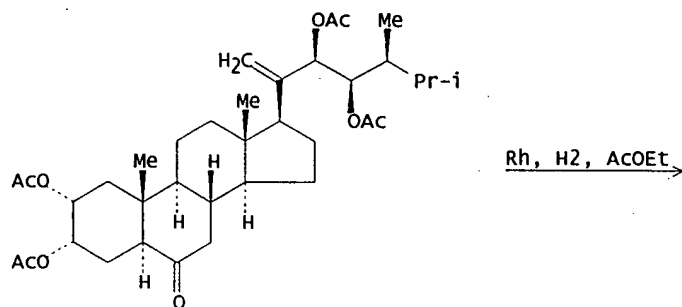
=> d bib abs fcdref 7

L45 ANSWER 7 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 108:187052 CASREACT
 TI An improved synthesis of plant growth regulating steroid brassinolide and its congeners
 AU Kametani, Tetsuji; Katoh, Tadashi; Fujio, Junko; Nogiwa, Ikuno; Tsubuki, Masayoshi; Honda, Toshio
 CS Inst. Med. Chem., Hoshi Univ., Tokyo, 142, Japan
 SO J. Org. Chem. (1988), 53(9), 1982-91
 CODEN: JOCEAH; ISSN: 0022-3263
 DT Journal
 LA English
 GI

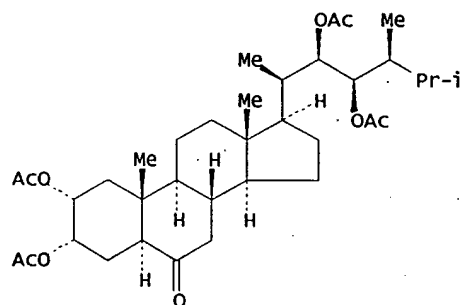
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AB Brassinosteroids including brassinolide (I) and castasterone (II) were prepd. from pregnenolone (III).

RX(41) OF 45



RX(41) OF 45



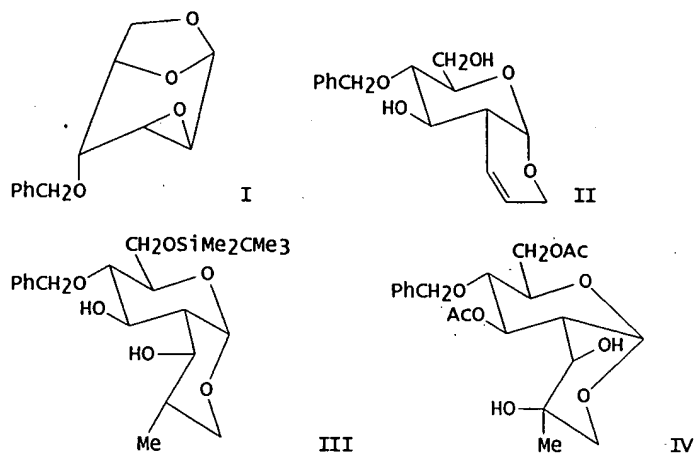
stereoisomers
47%

REF: J. Org. Chem., 53(9), 1982-91; 1988

OF 11 CASREACT COPYRIGHT 2001 ACS

=> d bib abs fcrdref 8

L45 ANSWER 8 OF 11 CASREACT COPYRIGHT 2001 ACS
 AN 107:154621 CASREACT
 TI Dipyranside precursors for ansamycins. Pyranosidic homologation. 5
 AU Fraser-Reid, Bert; Magdzinski, Leon; Molino, Bruce F.; Mootoo, David R.
 CS Paul M. Gross Chem. Lab., Duke Univ., Durham, NC, 27706, USA
 SO J. Org. Chem. (1987), 52(20), 4495-504
 CODEN: JOCEAH; ISSN: 0022-3263
 DT Journal
 LA English
 GI



AB The process of pyranosidic homologation was applied to the readily obtainable dianhydro sugar I in the context of prepn. of precursors for mols. contg. multiple contiguous chiral centers (e.g., the ansa chains of rifamycin S and streptovaricin A). Two approaches for construction of the lower satellites were detd. The first involved opening of the epoxide I with a carbanion derived from propargyl alc., followed by Lindlar redn. Treatment of the resulting allylic alc. with CF₃CO₂H lead to internal glycosidation; the cis-fused (i.e., .alpha.) bicyclic system II being highly favored. II on sequential silylation, epoxidn., epoxide ring cleavage with LiMe₂C₄, pyridinium chlorochromate oxidn., and LiAlH₄ redn. gave III the precursor for rifamycin S. Also prepd. from I was IV, required for streptovaricin A.

WADE, L. G.
Organic chemistry/L. G. Wade, Jr.—3rd ed.

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Includes index.

ISBN 0-13-301631-5

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L13 ANSWER 2 OF 6 HCAPLUS COPYRIGHT 2001 ACS
 AN 1992:257819 HCAPLUS
 DN 116:257819
 TI Kinetic and potentiometric studies of the hydrogenation of allyl esters of some fatty acids
 AU Il'khamdzhano, P.; Mirkamilov, T. M.; Makhmudova, Z.; Makhsumov, A. G.
 CS Tashk. Politekh. Inst., Tashkent, USSR
 SO Uzb. Khim. Zh. (1991), (6), 24-7
 CODEN: UZKZAC; ISSN: 0042-1707
 DT Journal
 LA Russian
 AB The H absorption rate and catalyst potential measured simultaneously in the liq.-phase, room-temp. hydrogenation of allyl laurate in the presence of Al-Ni catalysts modified with different metals (Na, K, Ti, Fe, Cu, Ca), a model reaction for hydrogenation of allyl esters of fatty acids, suggested that allyl esters are readily hydrogenated by these catalysts, although at different satn. rates. The highest activities, in descending rate order, were exhibited by catalysts contg. Na, K, and Ti. Catalyst amts. >1.5 mL per 0.005 g-mol ester did not affect the reaction rate.

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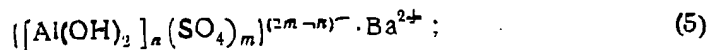
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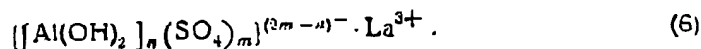
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где $m > n/2$.

На отрицательно заряженной поверхности модифицированного оксида алюминия катионы бария и лантана сорбируются по ионообменному механизму:



и



Разделение бария и лантана обусловлено, вероятно, различными значениями произведений растворимости (ПР) их сульфатных соединений: $1,1 \cdot 10^{-10}$ и $3,0 \cdot 10^{-5}$ для сульфатов бария и лантана соответственно [6].

Различное распределение одного и того же иона в верхнем и нижнем слоях хроматографической колонки объясняется исходящим принципом динамической сорбции, когда сорбент насыщается с верхних слоев к нижним. Из-за неполного насыщения сорбента в процессе разделения элементов (а это противоречит одному из основных условий) основная часть бария сорбируется в верхних слоях хроматографической колонки. Коэффициенты же распределения лантана невысокие. Поэтому при пропускании его раствора через колонку в объеме более трех колоночных лантан в процессе перемещения частично удерживается в нижних слоях.

Таким образом, наиболее перспективной для разделения бария и лантана является система из модифицированного оксида алюминия. Она может быть использована как сорбент для закрепления материнского нуклида Ba-140 высокой удельной активности при создании генератора La-140.

ИСПОЛЬЗОВАННАЯ ЛИТЕРАТУРА

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Институт ядерной физики
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П. ИЛЬХАМДЖАНОВ, Т. М. МИРКАМИЛОВ, З. МАХМУДОВА, А. Г. МАХСУМОВ КИНЕТИЧЕСКИЕ И ПОТЕНЦИОМЕТРИЧЕСКИЕ ИССЛЕДОВАНИЯ ПРОЦЕССА ГИДРИРОВАНИЯ АЛЛИЛОВЫХ ЭФИРОВ НЕКОТОРЫХ ЖИРНЫХ КИСЛОТ

Приведены результаты гидрирования аллиловых эфиров на скелетных никелевых катализаторах. Показана различная активность катализаторов. Установлено количество водорода, поглощаемого отдельными эфирами, и подтверждено, что катализаторы способны гидрировать исследуемые эфиры до полного насыщения.

Ранее [1] мы исследовали синтез аллиловых эфиров карбоновых кислот C_2-C_{18} и их гидрирование в присутствии никель-скелетных катализаторов. В настоящей статье приводим кинетические и потенциометрические кривые гидрирования аллилового эфира лауриновой

кислоты на скелетных никелевых катализаторах, содержащих добавки натрия, калия, титана, железа, меди и кальция.

Гидрирование проводили в жидкой фазе по методике [2] при комнатной температуре, одновременно измеряя скорость поглощения водорода и потенциал катализатора.

Установлено, что аллиловые эфиры на этих катализаторах гидрируются сравнительно легко, но с различной скоростью насыщения.

Состав приготовленных сплавов

Катализатор	Сплав	Компоненты сплава, мас. %		
		Ni	Модификатор металла	Al
1	Ni-Na-Al	48	2	50
2	Ni-K-Al	48	2	50
3	Ni-Ti-Al (промышл.)	47	3	50
4	Ni-Fe-Al (промышл.)	47	3	50
5	Ni-Cu-Al (промышл.)	45	5	50
6	Ni-Sn-Al	45	5	50
7	Ni-Sn-Al (промышл.)	25	25	50

На рис. 1 представлены кинетические и потенциометрические кривые гидрирования аллилаурата в этаноле на исследуемых катализаторах.

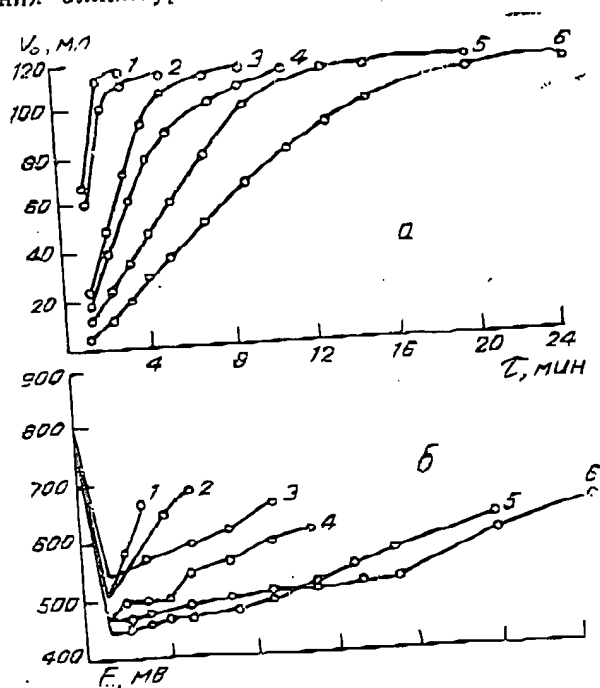


Рис. 1. Кинетические и потенциометрические кривые гидрирования аллилового эфира лауриновой кислоты на скелетном никеле с различными добавками. Условия: эфир — лауриновой кислоты — 20 мл, катализатор — 1 мл, температура — 20°C, число качаний утки 300—350 в мин.

торах. Самую высокую активность проявили катализаторы Ni-Na-Al и Ni-K-Al, а из промышленных — Ni-Ti-Al. Высокая активность катализаторов №1 и 2 обусловлена, по-ви-

димому, наличием щелочного компонента: щелочной металл в составе никелевых катализаторов повышает их активность и способствует стабилизации [3].

По данным потенциометрических кривых гидрирования, введение эфира в реакционную систему смещает потенциал катализатора от обратимого водородного потенциала в анодную сторону на величину, зависящую от природы взятого в реакцию вещества и его количества. Молекулы эфиров, адсорбируясь на поверхности катализатора, вытесняют из него водород, изменяя тем самым его потенциал. При этом, естественно, нарушается равновесие между водородом, адсорбированным на поверхности катализатора, и водородом газовой фазы, устанавливаемое в процессе насыщения катализатора до обратимого водородного потенциала. С первых минут после начала встряхивания, как видно из потенциометрической кривой аллилового эфира, вследствие донасыщения катализатора водородом, потенциал поднимается с раз-

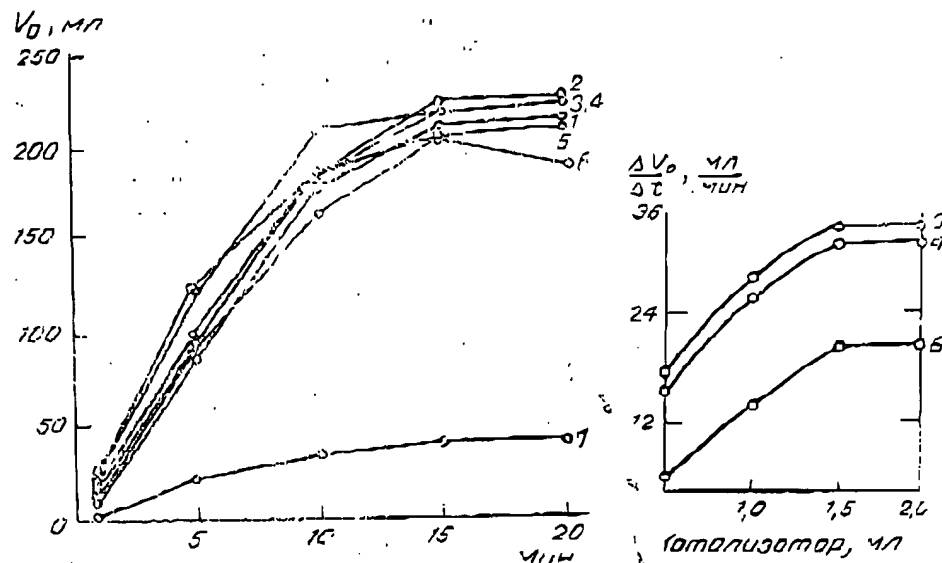


Рис. 2. Зависимость степени насыщения аллилкапроната от температуры гидрирования (Условия те же, что рис. 1).

1 — 10, 2 — 20, 3 — 30, 4 — 40, 5 — 50, 6 — 60, 7 — 70°C.

Рис. 3. Влияние количества катализатора на скорость гидрирования аллилового эфира капроновой кислоты. Условия: эфир — 0,780 г (остальное, как на рис. 1).

личной скоростью до конца гидрирования аллилового эфира, но не достигает значения обратимого водородного потенциала. Разность между значениями потенциала катализатора в конце реакции и обратимым водородным тем меньше, чем выше исходная активность катализатора.

С повышением температуры реакции общее количество поглощенного водорода уменьшается, а продолжительность гидрогенизации при этом остается постоянной (рис. 2). Максимальный объем водорода поглощается при 20—40°C. Следовательно, опыты целесообразно проводить при комнатной температуре.

Несмотря на различную активность катализаторов, общее количество поглощенного водорода в отдельных эфирах примерно одинаково, т. е. взятые катализаторы способны гидрировать исследуемые эфиры до одинаковой степени насыщения. Мы выбрали экономичный и

наиболее доступный катализатор № 3, используемый в промышленности.

В последующих опытах было изучено влияние количества катализатора на скорость гидрирования аллилкапроната в этаноле. Соотношение количества катализатора и скорости гидрогенизации в жидкой фазе определено в [4]. Есть мнение [5], что при низких температурах скорость гидрирования пропорциональна количеству катализатора, а при высоких температурах — стремится к пределу.

Установлено, что скорость гидрирования в спиртовой среде эфиров высокомолекулярных жирных кислот различной степени непереносимости при температуре ниже 60°C пропорциональна количеству катализатора [6]. Для экспериментов мы брали по 0,5—2,0 мл катализатора на 0,005 г-моль эфира при температуре 40°C.

С увеличением количества катализатора (рис. 3) от 0,5 до 2,0 мл скорость поглощения водорода возрастает. Сначала она растет пропорционально количеству катализатора до максимума при содержании 1,5 мл скелетного никеля. Увеличение же количества катализатора не влияет на скорость насыщения эфира, так как в этом случае активная поверхность катализатора, участвующая в гидрогенизации в данный момент, не увеличивается.

Можно заключить, что аллиловые эфиры жирных кислот легко гидрируются в присутствии никелевых катализаторов с добавками щелочных металлов при комнатной температуре. При этом катализатор в количестве более 1,5 мл на 0,005 г-моль не влияет на скорость реакции.

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М. Г. ХОДЖАЕВА, Б. Г. ИСХАКОВ, Н. Н. АБДУСАЛЯМОВ, Т. С. ИСМАИЛОВ
ТЕПЛОЕМКОСТЬ И ТЕРМОДИНАМИКА 2,4,6-ТРИМЕТИЛФЕНОЛА

Изучены термодинамические свойства 2,4,6-триметилфенола, являющегося полупродуктом производства витамина Е.

Выпуск лекарственных препаратов, внедрение новых технологий в производство во многом зависят от степени изученности физико-химических свойств компонентов, задействованных в конкретном технологическом процессе.

Мы изучали термодинамические и термохимические свойства 2,4,6-триметилфенола — одного из исходных компонентов синтеза триметилгидрохинона, участвующего в синтезе α-токоферилацетата (вита-

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silica supported palladium-copper catalysts were obtained in a fast and simple prepn. method by reduct. of bimetallic organometallic compds. on the support surface in the liq. phase at room temp. The supported bimetallic particles were analyzed by TEM and EDAX. Directly after prepn. the silica supported palladium-copper catalysts could be used in the semihydrogenation of triple bonds. The catalysts are selective in the hydrogenation of acetylenes and propargylic alcs. giving high yields of either olefins or satd. hydrocarbons, depending on reaction time. In addn., the catalytic system shows reasonable selectivity towards cis-olefins in the hydrogenation of disubstituted acetylenes.

Remarks:

IT 7440-05-3DP, Palladium, silica-bound
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
USES (Uses)

(prepn. of silica-supported bimetallic palladium-copper catalysts for the chemo- and stereoselective hydrogenation of alkynes and alkynols)

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313

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Simple preparation of bimetallic palladium-copper catalysts for selective liquid phase semihydrogenation of functionalized acetylenes and propargylic alcohols

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Silica supported palladium-copper catalysts were obtained in a fast and simple preparation method by reduction of bimetallic organometallic compounds on the support surface in the liquid phase at room temperature. The supported bimetallic particles were analysed by TEM and EDAX. Directly after preparation the silica supported palladium-copper catalysts could be used in the semihydrogenation of triple bonds. The catalysts are selective in the hydrogenation of acetylenes and propargylic alcohols giving high yields of either olefins or saturated hydrocarbons, depending on reaction time. In addition, the catalytic system shows reasonable selectivity towards *cis*-olefins in the hydrogenation of disubstituted acetylenes.

1. INTRODUCTION

Catalytic liquid phase semihydrogenation of acetylenes is an important industrial and laboratory reaction, especially in fine chemical synthesis [1]. The use of supported metal catalysts for this selective hydrogenation readily facilitates the separation of organic products from the catalyst. However, liquid phase reactions with supported catalysts tend towards mass transport limitation [2] and, therefore, the support particles should be between 1 and 10 μm in size; this avoids transport limitations and separation problems. With support particles of this size high temperature reduction in a flow of H_2 gas is very difficult and to avoid this step it is possible to prepare supported metal particles by decomposing organometallic compounds under mild conditions [3-5].

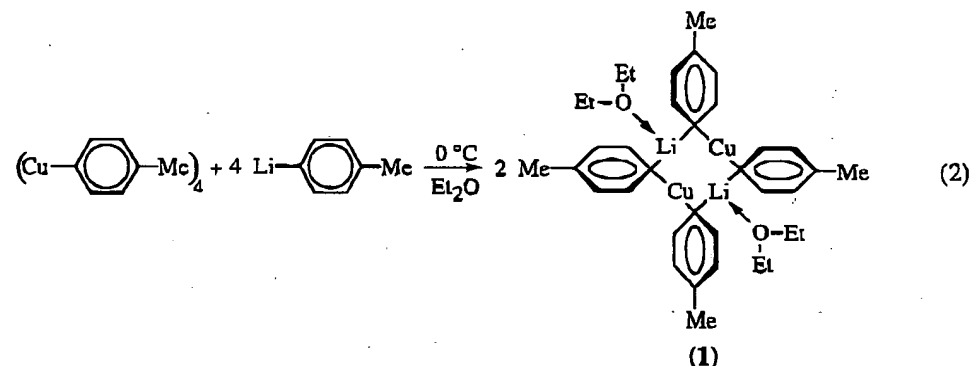
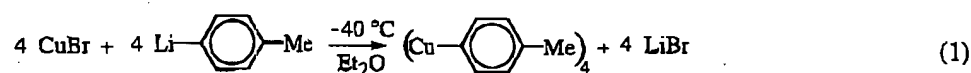
As part of a major research topic concerning characterization and mode of operation of novel (bi-)metallic catalysts for liquid phase catalysis, we have now developed a fast and simple preparation method for supported bimetallic catalysts, even of less noble metals. This method involves reduction of bimetallic

organometallic compounds on the support surface in the liquid phase at room temperature. This method has been used to prepare silica supported palladium-copper catalysts (Pd/Cu/SiO₂) which were tested in the liquid phase semihydrogenation of functionalized acetylenes and propargylic alcohols.

2. RESULTS AND DISCUSSION

2.1. Catalyst preparation

The organometallic copper precursor is synthesized in two steps. First *p*-tolylcopper, Cu(*p*-tolyl), is prepared from *p*-tolyllithium and copper(I) bromide in diethyl ether. Reaction between *p*-tolylcopper and a second equivalent of *p*-tolyllithium affords the cuprate [6-8]. (See equations 1-2.)



Addition of a toluene solution of the cuprate, Cu₂Li₂(*p*-tolyl)₄·2Et₂O (1), to a solution of palladium(II) acetate in toluene leads to the *in situ* formation of a thermally unstable organocopper complex in which the lithium atom of 1 has been replaced by the more electronegative precious metal. Subsequent reductive elimination of the organic tolyl group from the unstable bimetallic complex in the presence of silica affords supported bimetallic particles, which without further treatment are an active catalytic system. (Equation 3)

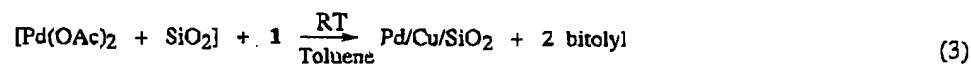
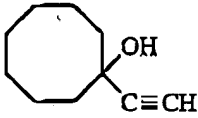
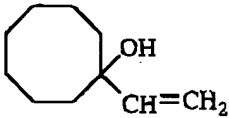


Table I.

Liquid phase semihydrogenation of monosubstituted acetylenes (5 mmol) catalysed by Pd(4 w%)/Cu(2 w%)/SiO₂ (circa 35 mg) in ethanol.

Substrate	t_{\max}^a (min)	Semihydrogenated product	Yield ^{b,c} (%)
$\text{Ph}-\text{C}\equiv\text{CH}$	5	$\text{Ph}-\text{CH}=\text{CH}_2$	95
$\begin{array}{c} \text{OH} \\ \\ \text{Me}-\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{Me} \end{array}$	11	$\begin{array}{c} \text{OH} \\ \\ \text{Me}-\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{Me} \end{array}$	98
$\begin{array}{c} \text{OH} \\ \\ \text{Et}-\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{Me} \end{array}$	2	$\begin{array}{c} \text{OH} \\ \\ \text{Et}-\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{Me} \end{array}$	97
$\begin{array}{c} \text{O} \quad \text{Me} \\ \quad \\ \text{Me}-\text{C}-\text{O}-\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{Et} \end{array}$	3	$\begin{array}{c} \text{O} \quad \text{Me} \\ \quad \\ \text{Me}-\text{C}-\text{O}-\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{Et} \end{array}$	95
	2		94

^aTime for maximum percentage of semihydrogenated compound. ^bYield at 100% alkyne conversion determined by G.C. peak area analysis. ^cIn all cases the by-product was the fully saturated compound.

2.2. Catalytic hydrogenations

To test the selectivity of the bimetallic system, monosubstituted acetylenes (Table I) and disubstituted acetylenes (Table II) were hydrogenated with the use of the silica supported palladium-copper catalysts. The yields of the olefins at 100% conversion of the acetylene are given. However, in all cases with longer hydrogenation times it was possible to end up with the fully saturated product.

Table II.

Liquid phase semihydrogenation of disubstituted acetylenes (5 mmol) catalysed by Pd(4 w%)/Cu(2 w%)/SiO₂ (circa 35 mg) in ethanol.

Substrate	t_{\max}^a (min)	Semihydrogenated product	Yield ^{b,c} (%)
Ph-C≡C-Ph	6	Ph-CH=CH-Ph	<i>cis</i> 85 <i>trans</i> 4
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{HO}-\text{C}-\text{C}\equiv\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	20	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{HO}-\text{C}-\text{CH}=\text{CH}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	<i>cis</i> 99 <i>trans</i> ^d
$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{C}\equiv\text{C}-\text{Ph} \\ \\ \text{Me} \end{array}$	3	$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{CH}=\text{CH}-\text{Ph} \\ \\ \text{Me} \end{array}$	<i>cis</i> 80 <i>trans</i> 3
$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{C}\equiv\text{C}-\text{Ph} \\ \\ \text{Ph} \end{array}$	5	$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{CH}=\text{CH}-\text{Ph} \\ \\ \text{Ph} \end{array}$	<i>cis</i> 88 <i>trans</i> ^d
$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-4\text{-OMe} \\ \\ \text{Ph} \end{array}$	6	$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-4\text{-OMe} \\ \\ \text{Ph} \end{array}$	<i>cis</i> 85 <i>trans</i> ^d

^aTime for maximum percentage of semihydrogenated compound. ^bYield at 100% alkyne conversion determined by G.C. peak area analysis. ^cIn all cases the by-product was the fully saturated compound. ^dNo *trans* isomer was detected.

2.3. Catalyst characterization

Transmission Electron Microscopy (TEM) measurements on the catalysts containing palladium and copper in a ratio of either 1:1 or 1:2 showed a good dispersion of the metal particles (2-5 nm) over the support. Energy Dispersive X-ray Analysis (EDAX) on the samples revealed the presence of both metals in each examined particle. By doubling the amount of copper a proportionate increase of copper content in the metal particles was detected as expected.

3. EXPERIMENTAL

3.1. General considerations

Reactions were performed in an atmosphere of dinitrogen using Schlenk techniques. Toluene, benzene, diethyl ether and pentane were freshly distilled from sodium benzophenone-ketyl. All other solvents were used as received.

The support material used was silica OX-50 (surface area 50 m²/g) which was purchased from Degussa. Before usage the silica was boiled in bi-distilled water and dried *in vacuo* at 200 °C for 3 d to increase the amount of silanol groups.

Pd(OAc)₂ (47.35 % Pd) was purchased from Degussa. The compounds 4-iodotoluene, n-butyllithium (1.6 M in hexane), 3-methyl-1-pentyn-3-ol, 2-butyne-1,4-diol, phenylacetylene, diphenylacetylene, 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyne-2-ol were obtained from Acros. Other propargylic alcohols were prepared according to the literature [9,10] and purified by kugelrohr distillation and crystallization. The substrates were analysed by G.C., G.C.M.S. and ¹H NMR and ¹³C NMR spectroscopy prior to use. Complex Cu₂Li₂(*p*-tolyl)₄(Et₂O)₂ was prepared according to literature procedures [3,4] and analysed by ¹H NMR spectroscopy.

The NMR spectra were recorded on Bruker AC200 (200 MHz) and AC300 (300 MHz) spectrometers at ambient temperature in NMR solvents obtained from ISOTEC Inc.. G.C. analysis were performed on Unicam PU4600 and PU610 apparatus with 30 m J&W Scientific DB-1, DB-17 and AT-SILAR capillary columns and flame ionization detectors. Product yields were determined by peak area analysis; response factors for selected substrates and products were found to be virtually identical. Internal standards were used in the initial stage of this study, but were found to influence the catalyst characteristics. G.C.M.S. was performed on a Unicam Automass apparatus combined with 610 series G.C. apparatus equipped with 30 m J&W Scientific DB-1 and DB-17 columns. TEM-EDAX was performed on a Phillips CM 200 microscope equipped with a field emission gun. TEM-EDAX samples were prepared by application of a few droplets of a suspension of the catalyst in ethanol onto a holey carbon film which was supported by a nickel grid after which the ethanol was allowed to evaporate.

3.2. Preparation of the copper precursor [Cu₂Li₂(*p*-tolyl)₄(Et₂O)₂]

Preparation of [Li(*p*-tolyl)]. To a solution of 8.76 g (40.2 mmol) 4-iodotoluene in *ca.* 30 mL toluene was added 1.05 equivalent of n-butyllithium at 0 °C. The resulting white suspension was stirred for 30 min., after which the slightly yellow solution was decanted. The white residue was washed with pentane (5 x 50 mL) and dried *in vacuo*. Prior to the next preparation step the white solid was dissolved in diethyl ether, centrifuged and decanted. After evaporation of the solvent a white solid was obtained. Yield 3.70 g (94%).

Preparation of [Cu₄(*p*-tolyl)₄]. To a suspension of 2.09 g (14.6 mmol) CuBr in diethyl ether was slowly added a solution of 1.47 g (15.0 mmol) *p*-tolylolithium in

ca. 15 mL diethyl ether at -78°C . After 1 h the suspension was allowed to warm to 0°C , after which the intense yellow precipitate was isolated by decantation, washed with cold (0°C) diethyl ether ($4 \times 50\text{ mL}$) and dried *in vacuo*. Yield 1.34 g (62%). ^1H NMR (C_6D_6 , 300 MHz): δ 8.02 (d, 8 H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, aryl), 6.86 (d, 8 H, $^3J_{\text{HH}} = 7.5\text{ Hz}$, aryl), 1.96 (s, 12 H, CH_3).

Preparation of $[\text{Cu}_2\text{Li}_2(p\text{-tolyl})_4(\text{Et}_2\text{O})_2]$. To a suspension of 0.70 g (5.0 mmol) *p*-tolylcopper in diethyl ether (25 mL) was slowly added a solution of 0.53 g (5.4 mmol) *p*-tolyllithium in diethyl ether (20 mL) at 0°C . The resulting greenish solution was stirred for 1 h during which time a white precipitate of the product formed. The solid was isolated by decantation, washed twice with pentane and recrystallized from diethyl ether. Yield 1.08 g (66%). ^1H NMR (C_6D_6 , 300 MHz): δ 8.37 (d, 8 H, $^3J_{\text{HH}} = 7.2\text{ Hz}$, aryl), 7.07 (d, 8 H, $^3J_{\text{HH}} = 7.2\text{ Hz}$, aryl), 2.78 (q, $^3J_{\text{HH}} = 7.2\text{ Hz}$, OCH_2CH_3), 2.12 (s, 12 H, CH_3), 0.74 (t, $^3J_{\text{HH}} = 7.2\text{ Hz}$, OCH_2CH_3).

3.3. Preparation of the supported palladium-copper catalysts

Silica supported catalysts with different metal loadings were prepared in several batches: Pd/Cu/ SiO_2 (4.0 w% Pd, 2.1 w% Cu; Pd:Cu = 1:1) (I), Pd/Cu/ SiO_2 (4.0 w% Pd, 4.2 w% Cu; Pd:Cu = 1:2) (II).

The catalysts were prepared in a reactor vessel of 250 mL. The reactor vessel was equipped with three baffles (120°) and mechanically stirred with a gas-circulating stirrer (2000 rpm). A red ultrasonically pre-treated solution of palladium(II) acetate in ca. 35 mL toluene was added to an ultrasonically pre-treated suspension of silica in ca. 150 mL toluene using a tube pump (Gilson Minipuls 2, equipped with a PVC tube, type GI 17942 internal diameter 1.52 mm and a Teflon injection tube, outer diameter 1.52 mm). The solution was injected at the height of the stirrer. The formed orange suspension was stirred for 24 h after which a yellow solution of the copper precursor in ca. 50 mL toluene was added by means of the tube pump. This resulted in a dark brown suspension. After stirring for 3 d, dihydrogen was introduced to the resulting black suspension during 3 h to be sure that the reduction process was completed. Stirring was stopped and the colourless solution was decanted from the settled material. The resulting black powder was washed twice with pentane and dried *in vacuo* at room temperature.

Both the activity and selectivity of all catalysts batches were tested in the hydrogenation of 3-methyl-1-pentyn-3-ol before use.

3.4 Catalytic hydrogenations

The hydrogenations were performed in a glass reactor vessel applied with a gas-circulating stirrer (2000 rpm) and three vertical glass baffles at atmospheric dihydrogen pressure. The reactor vessel was kept at 25°C by circulating thermostated water through the wall of the vessel. In all hydrogenation reactions

the following procedure was executed. The reactor vessel was evacuated and filled with dinitrogen. The catalyst (ca. 35 mg) was added to the reactor followed by addition of 100 mL of ethanol. While stirring the (nitrogen) atmosphere was expelled out of the equipment by subsequent evacuation and flushing with dihydrogen (5x). The suspension was stirred for 1 h under dihydrogen. Next, without stirring, a solution of the substrate (5 mmol) in 1.5 mL ethanol was added with a hypodermic syringe. After the first sample had been taken the hydrogenation reaction was started by switching the stirring device on.

Dihydrogen uptake was monitored using a gas burette system. G.C.(M.S.) samples were taken through a silicon septum with a hypodermic syringe. Substrates and products were analysed with G.C. and confirmed with G.C.M.S..

4. CONCLUSIONS

The method described allows fast and consistent production of silica supported bimetallic palladium-copper catalysts in the liquid phase at room temperature, without the need for high temperature reduction. The catalysts show homogeneous dispersion of the mixed metal particles over the support surface and are ready to use immediately after preparation.

The silica supported palladium-copper catalysts are selective in the hydrogenation of monosubstituted acetylenes giving high yields of either olefins or saturated hydrocarbons, depending on the reaction time. In addition, the catalytic system shows reasonable selectivity towards *cis*-olefins in the hydrogenation of disubstituted acetylenes.

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DN 87:22319
TI Study of the hydrogenation of allyl esters of aliphatic acids on different industrial Raney nickel catalysts
AU Il'khamdzhanov, P.; Makhsumov, A. G.; Makhmudova, Z.; Abdurakhimov, A.
CS USSR
SO Deposited Doc. (1975), VINITI 111-75, 8 pp. Avail.: 8LLD
DT Report
LA Russian
AB Ni-Al catalysts contg. Na or K were more active in the hydrogenation of allyl laurate than Ni-Al catalysts contg. Ti, Fe, Cu, or Ca. In the hydrogenation of allyl caproate the rate increased with increasing amt. of catalyst and then leveled off at the same point for Ni-Ti-Al, Ni-Fe-Al, and Ni-Cu-Al catalysts.

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П. Ильхамджанов, А.Г.Махсумов, Э. Махмудова,
А. Абдурахимов.

ИССЛЕДОВАНИЕ ПРОЦЕССА ГИДРОГЕНИЗАЦИИ
АЛКИЛОВЫХ ЭФИРОВ ЖИРНЫХ КИСЛОТ НА
РАЗЛИЧНЫХ ПРОМЫШЛЕННЫХ СКЕЛЕТНЫХ НИ-
КЕЛЕВЫХ КАТАЛИЗАТОРАХ.

Untersuchung des Hydrogenierungs-
von Fettsäurealkylethern an
an verschiedene industrielle
Nickel-skelettkatalysatoren.

Т а ш к е н т - 1975 г.

В литературе имеется изобилие работ по гидрированию непредельных органических соединений. Использовались никель-скелетные, платиновые и палладиевые катализаторы на исследованиях /1-2-3/.

Однако, гидрирование аллиловых эфиров жирных кислот на скелетных катализаторах совершенно не изучено.

В предыдущей работе / 4 / нами приведены результаты синтеза и некоторые вопросы гидрирования аллиловых эфиров карбоновых кислот в присутствии никель-скелетных катализаторов. В настоящей работе мы исследовали гидрирование аллилового эфира на скелетных никелевых катализаторах содержащих добавки натрия калия, титана, железа, меди и кальция.

Эксперименты проводили в каталитической утке, согласно методике, разработанной Д.В.Сокольским и др. /5/, при температуре 20-22°C с одновременным измерением скорости поглощения водорода и потенциала катализатора.

Полученные результаты показывают, что аллиловые эфиры на этих катализаторах гидрируются сравнительно легко, но с различной степенью насыщения.

На рис. I представлены кинетические и потенциометрические кривые гидрирования аллиллауриата в эталоне на указанных скелетных катализаторах. Как видно из графика на никель-натрий-алюминиевом и никель-калий-алюминиевом катализаторах насыщение двойной связи завершается за 3 и 5 минуты, в то время, как в присутствии $Ni-Ti-Al$, $Ni-Fe-Al$, $Ni-Cu-Al$, $Ni-Ca-Al$, - катализаторов процесс заканчивается соответ-

венно за 9, 11, 20 и 25 минут. Из графика видно, что самую высокую активность проявили катализаторы $Ni-Na-Al$ =48:2:50 и $Ni-K-Al$ =48:2:50;

Анализ потенциальных кривых показывает, что введение эфира в реакционную систему смещает потенциал катализатора в анодную сторону от обратимого водородного потенциала. Различия в величинах смещения потенциала зависят от природы катализатора. Молекулы эфира адсорбируясь на поверхности катализатора, вытесняют водород, смещая тем самым потенциал катализатора. При этом, естественно, нарушается равновесие между водородом, адсорбированным на поверхности катализатора и водородом газовой фазы, которое установилось в процессе насыщения катализатора до обратимого водородного потенциала. С первых минут после начала встряхивания, как видно из потенциальной кривой аллилового эфира, вследствие донирования катализатора водородом потенциал сразу начинает подниматься с различной скоростью до конца гидрирования аллилового эфира, но не достигает значения обратимого водородного потенциала. Разность между значением потенциала катализатора в конце реакции и обратимым водородным тем меньше, чем выше исходная активность катализатора.

Обобщенные данные о зависимости скорости гидрирования аллиловых эфиров карбоновых кислот от количества скелетных никелей приведены на рис. 2. Видно, что скорость реакции гидрирования сначала растет пропорционально количеству катализатора и достигает наивысшей скорости при содержании 1,5 мл. ске-

летного никеля, а дальнейшее увеличение количества катализатора не влияет на скорость насыщения эфира.

ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ.

В каталитическую "утку" загружали катализатор в абсолютном эталоне. Вок систему продували электрическим подородом. Затем при сильном встряхивании при температуре опыта катализатор донасыщали в течении 20-25 мин. К насыщенному катализатору, находящемуся в утке, через воронку в токе водорода добавляли навеску исследуемого эфира и сразу же приводили в движение встряхивающий аппарат.

Количество поглощенного водорода постоянно измеряли от начала до полного прекращения реакции, фиксируя при этом изменение потенциала катализатора в период гидрирования.

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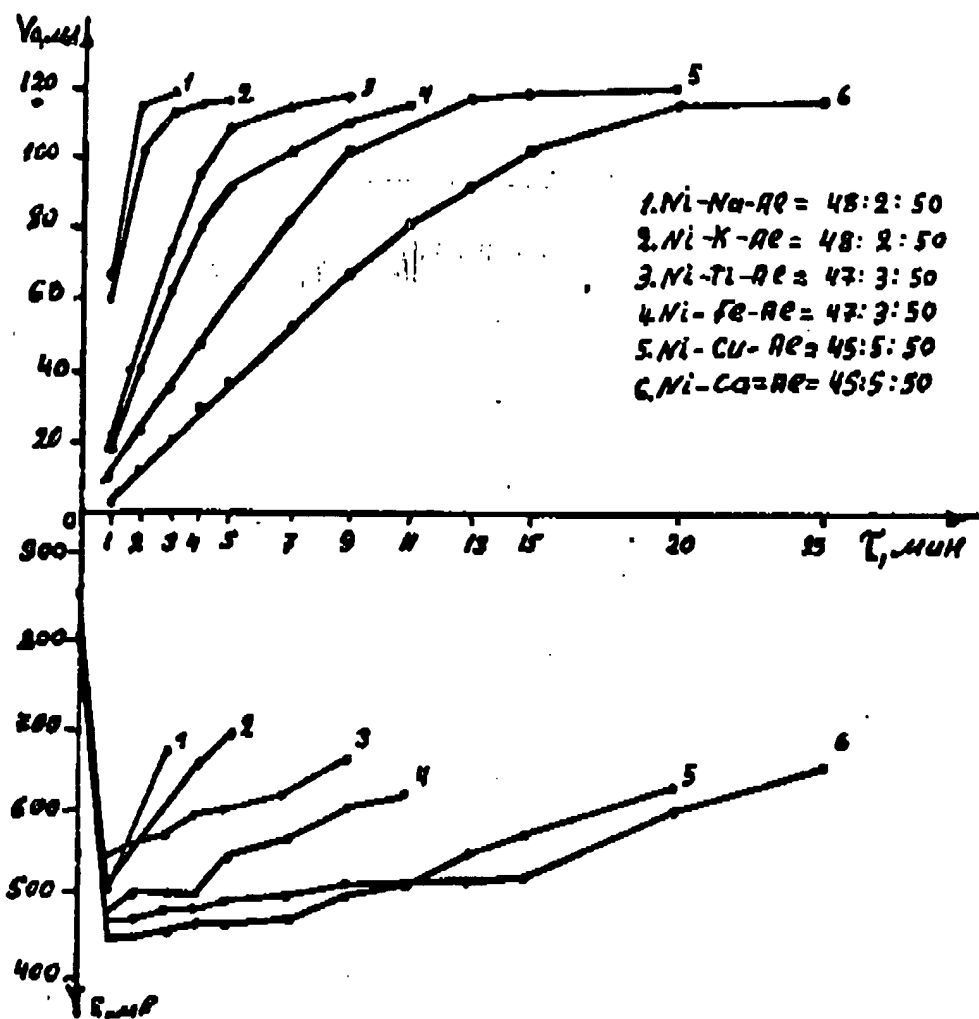


Рис. I. Кинетические и потенциметрические кривые гидролиза аллилового эфира лауриновой кислоты на скелетном никеле с различными добавками. Условия: Эфир - 1,2г; растворитель - абс.этиловый спирт - 20 мл; катализатор - 1 мл; тем-ра - 20°C ; число качаний утки 300-350 в мин.

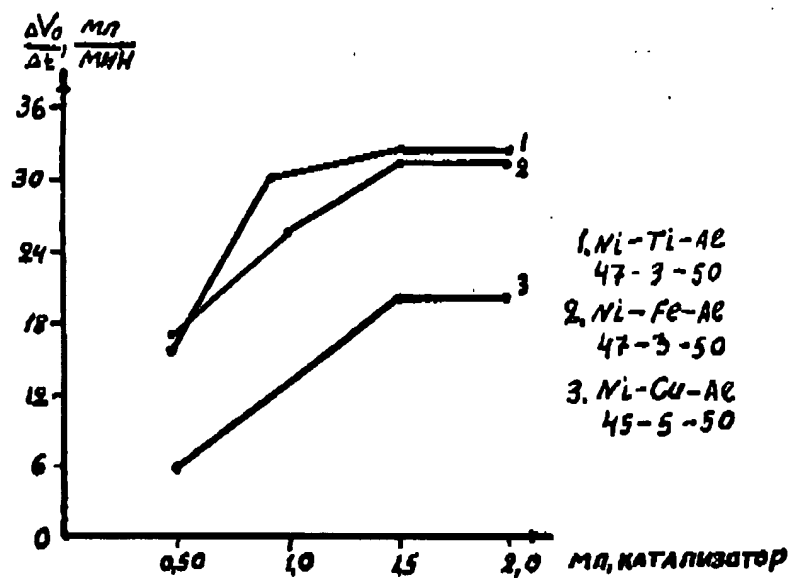


Рис. 2. Влияние количества катализатора на скорость гидрирования аллилового эфира капроновой кислоты.
Условия: эфир— 0,760 г; остальные как на рис. I.

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Volume (Issue):	AU Makhmudova, Z.; Il'khamdzhanov, I. P.; Abdurakhimov, A. CS USSR SO Tr. Tashk. Politekh. Inst. (1974), 119, 117-19 CODEN: TTPLAA
Pages:	DT Journal LA Russian AB The title process in the presence of Raney Ni-Al-Ti (47:50:3) was independent of temp. >40.degree.; optimum conditions included MeOH, EtOH, hexane, or ligroine as solvent at 20-30.degree..
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Как видно из таблицы, у перэтерификата значительно снижается температура плавления и твердость.

Горячий жир имеет кремово-желтый цвет, запах жира напоминает запах парного молока.

Цвет перэтерификата, имевший желтоватый оттенок, после процесса перэтерификации становится более светлым. После перэтерификации перэтерификат теряет запах парного молока и приобретает совершенно однородный характер.

Кроме того, диатометрический анализ подтверждает, что в ходе перэтерификации происходит снижение количества твердой фазы при температуре 20°C и равномерное ее распределение в жире. При застывании в условиях комнатной температуры эти смеси не расслаиваются. Все они застывают однородно, без выделения легкой фракции.

Жировая основа, полученная путем перэтерификации смеси говяжьего жира и хлопкового масла при соотношениях 50:50 мл и 40:60 мл, по своим константам соответствует тресованному, представляемому к жировому сырью для производства маргарина.

М. Махмудова, З. Ибрагимов, А. Абдурахимов, СССР

ГИДРОГЕНИЗАЦИЯ АЛЛИЛОВЫХ ЭФИРОВ ЖИРНЫХ КИСЛОТ НА ПРОМЫШЛЕННОМ КАТАЛИЗАТОРЕ

Гидрирование органических соединений в растворителях на скелетных катализаторах представляет большой интерес. Известно гидрирование аллиловых эфиров кротеновой, фумаровой и оксалиновой кислот в присутствии палладиевых и платиновых катализаторов [1]. Однако, палладиевые и платиновые катализаторы из-за дороговизны практически не находят промышленного применения. Нами осуществлен синтез и гидрирование аллиловых эфиров карбоновых кислот гомологического ряда, начиная от уксусной, кончая стеариновой кислотой и аллилолеата на промышленном оксидном никель-алюминиевом катализаторе, промотированном титаном. Изучал процесс гидрирования аллиловых эфиров жирных

Hydrogenation of the allyl esters of fatty acids on industrial catalysts.

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комнатой
и Пони
окорота

1. В.П.Г
2. А.В.С

кислот на этом катализаторе, мы определяли влияние температуры и растворителя на скорость реакции насыщения. В результате найдены оптимальные условия влияния этих факторов на процесс гидрогенизации.

Гидрирование аллиловых эфиров жирных кислот в растворителях на скелетном $Ni-Al-Ti$ (47-50-3) катализаторе проводили на установке для каталитического гидрирования в жидкой фазе [2,3]. Приготовление $Ni-Al-Ti$ (47-50-3) катализатора и его активизацию производили согласно действующей методике [4].

Исследуя влияние различных растворителей на скорость гидрирования аллиловых эфиров жирных кислот. Установили, что хорошими растворителями в ряду одноатомных алкаголей являются метиловый и этиловый спирты. С увеличением углеводородного радикала спирта скорость гидрирования постепенно падает, что связано, вероятно, с их растворяющей способностью. Для сравнения гидрирования были проведены опыты в неполярных растворителях: в гексане и бензине. Было выявлено, что бензин и гексан также являются хорошими растворителями для проведения реакции гидрогенизации аллиловых эфиров жирных кислот. Максимальная скорость гидрогенизации в этих растворителях близка к скорости насыщения в среде этанола и атанола.

Изучая влияние различных температур на скорость процесса, мы пришли к выводу, что температура играет определенную роль в реакции гидрогенизации.

Общее количество поглощенного водорода при 20 и 30°C больше, чем при температурах более 40°C. Следовательно, дальнейшие опыты целесообразно проводить при 20-30°C, т.е. при комнатной температуре.

Повышение температуры реакции не влияет на максимальную скорость поглощения водорода и на время гидрогенизации.

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3. А.В.Сокольский, Ф.Г.Голодов, Л.С.Голодова, Е.Г.Болховитина. Исследование катализаторов гидрогенизации жиров, Ашха-Ата, 1958.
4. Руководство по методам исследования и техно-химическому контролю и учету производства в маслохлебо-вой промышленности. Том II, М., 1964.

А.С.Саидакмедов

ХРАНЕНИЕ СВЕЖИХ ТОМАТОВ ПРИ СУБКРИОСТАТИЧЕСКИХ ТЕМПЕРАТУРАХ

Изучение резистентности свежих томатов к действию низких температур позволило установить возможность хранения томатов (сортов Рома и Етамбовый) в переохлажденном или частично подмороженном состоянии при температурах $-2-3^{\circ}\text{C}$.

Постепенное снижение температуры среды способствует адаптации томатов к низким температурам. Адаптационный процесс сопровождается глубокой внутренней перестройкой клеточных структур томата, в результате чего адаптированные томаты безболезненно переносят более низкие температуры хранения. При медленном оттаивании адаптированных томатов в достаточной степени восстанавливаются свойства и качества свежих томатов.

Результаты полупромышленного хранения предварительно адаптированных свежих томатов показали пригодность такого режима обработки. При этом естественные потери резко снижаются, микробная порча томата уменьшается, возможные сроки хранения овощей увеличиваются до 30-40 дней.

Оценка качества томатов до и после обработки и хранения проводилась органолептически и физико-химическими методами.

Из данных таблицы видно, что хранение томатов (сортов Рома и Етамбовый) при криостатических температурах до 30-40 дней позволяет в достаточной мере сохранить витамин С.

Ⓢ Saidakhmedov, A.S.

Ⓢ USSR

Имя: _____
Фамилия: _____
Сорт: _____
Рома
Етамбовый
Т.А.Аб:
ИНТЕРСНИ

Восточн:
получают из
низкие прох
от, и остает
в основном у
кошки и аз
угливание.

Вторичн
и в низком
продукты раз
элементов во
зависимое от
ривания и т.д.

Для мит
работали схе
рок при очис

Общезве
механической
обменной емк
ность исполь
является эффе

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- Ⓢ Abdullayev, T
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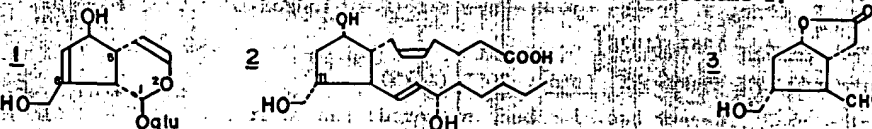
CHIRAL PROSTANOID INTERMEDIATES FROM AUCUBIN

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Summary: Several potentially useful prostanoid intermediates have been prepared from aucubin.

Dry DMSO-NBS converts enol ethers to α -bromoesters in one step.

Ohno and coworkers quite recently reported their ingenious conversion of aucubin (1) to (+)-11-deoxy-11 α -hydroxymethyl prostaglandin F_{2 α} (2).¹⁻⁴ As we have been pursuing an alternate path to the same goal, we would like to report our progress. Our primary target is the homolog (3) of the well-known Corey lactone-aldehyde, and the work is summarized in Scheme 1.



Schmid⁶ devised a four-step procedure for the conversion of aucubin (1) to lactone-hexa-acetate (7). This involved: 1) acetylation to 4; 2) conversion to bromohydrin (bromohemiacetal) 5 (mp 151°C) with Br₂-H₂O/THF; 3) oxidation (CrO₃/HOAc) to bromolactone 6 (mp 166°C); and 4) reduction (Zn/HOAc) to lactone 7 (mp 175°C).⁶ In our hands, steps 2 and 3 gave poor yields (35 and 50% respectively).

To improve step 2 we tried Dalton's procedure (NBS-H₂O/DMSO), which converted 4 to a mixture of three bromohydrins (HPLC showed 8, 3 parts and 9a+9b, 1 part; total yield 95%), from which 8 (mp 136°C) crystallized in 65% yield. Jones oxidation of 8 gave an excellent yield of the same bromolactone obtained previously from 5 (proving thereby that 5 and 8 are hydroxyl epimers).

Bromohydrins 9a and 9b proved to be inseparable, and therefore the crude mother liquors remaining after separation of 8 were oxidized (Jones) directly, affording an excellent yield of a second bromolactone, 10 (mp 123°C) (proving thereby that 9a and 9b are also hydroxyl epimers).

Both bromolactones 6 and 10 were reduced by Zn/HOAc to lactone 7 (proving thereby that they are bromine epimers).

We subsequently discovered that the use of dry DMSO (distilled from CaH₂) with NBS gave, in 90% yield, a mixture of bromolactones 6 and 10 (3:1, resp.) directly from 4.⁸ (Direct reduction of this mixture gave 7 in 90% yield.) Application of this new reaction to dihydropyran gave α -bromo- δ -valerolactone (62%); cyclohexene gave α -bromocyclohexanone (63%).

Hydrogenation of 7 over PtO₂ or Pd/C in EtOAc, EtOH, HOAc, dioxane or water (or mixtures), at -25 to 25°C and 1 to 100 atm., gave mainly products with extensive hydrogenolysis of the allylic acetate groups. On the other hand, hydrogenation of 7 over 5% Rh/C, in EtOAc at 4 atm., gave a 1:1 mixture of 11 and 12 (95% total). At 1 atm., 11 and 12 were formed in a 1:4 ratio (95%), and pure 12 crystallized directly from the reaction mixture in over 75% yield.

Methanolysis of epimer 12 gave only lactol 15 (82%) (with no trace of aldehyde 16 evident by NMR). On the other hand, 11 gave a mixture of lactol 14 (28%) and aldehyde 13 (50%), separated by preparative HPLC. In order to determine the relative orientation of the hydroxymethyl side chain,

lactols 14 and 15 were oxidized (Jones), respectively, to keto-lactones 17 (20%) and 18 (95%). The structures of 17 and 18 were confirmed by X-ray analysis, kindly performed by Dr. John Blount (Hoffmann-LaRoche). The absolute stereochemistry of these compounds is inferred from that of aucubin. 11 and 15 is the same (at iridoid C-5) as that of the prostanoids (at prostanoid C-8). Aucubin was isolated from *Aucuba japonica* by the procedure of Duff¹³; hot water extraction concentration in vac. and partition chromatography on Celite with water-saturated n-butanol. We have easily accumulated over 500 g. of aucubin by this method (1% of fresh plant weight).

At present we are attempting the conversion of 13 to 3 by inversion of the secondary hydroxyl group and subsequent lactone ring closure. A similar sequence applied to 15 should afford the β epimer of 3.

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 - 8) Details of the scope and mechanism of this new reaction are presently under investigation.
 - 9) Hydrogenation over Ru in wet EtOAc at 100 atm., or with Rh/Al₂O₃ in EtOAc at 1 atm. gave results similar to those obtained with Rh/C.
 - 10) Lactol 14 was oxidized with partial epimerization: Hplc separated 17 from the enantiomer of 18 (15%).
 - 11) J.M. Bobbitt and K.P. Segebarth, "The Iridoid Glucosides and Similar Substances", Chapter 1 in "Cyclopentanoid Terpene Derivatives", W.I. Taylor and A.R. Batterby, editors (Marcel Dekker, N.Y., 1969).
 - 12) We extracted leaves, twigs etc., obtained by pruning adult plants. *Aucuba japonica* is a very common plant. Our source: Ingleside Plantation Nurseries, Oak Grove, Westmoreland County, Va.
 - 13) R.B. Duff et al., *Biochem. J.*, **96**, 1 (1965).
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 - 15) A.J. Birch, J. Grimshaw and H.R. Juneja, *J. Chem. Soc.*, 5194 (1961).
 - 16) This compound gave a satisfactory elemental analysis.
 - 17) High Field NMR spectra were obtained at the Southern New England High Field NMR Facility at Yale University (270Mc) or at Rockefeller University (220Mc).
 - 18) Ms. B. DeBarbieri (Hoffmann-LaRoche) was the gracious source of the high-resolution mass spectra. Medium resolution (CI) spectra were obtained at Rockefeller University.
- We gratefully acknowledge the support of NIH grant GM-22098 and CUNY grant 11088. In addition the high pressure and large scale hydrogenations performed by Dr. William Jones (Merck) were of invaluable assistance.

Compound	Best Yield	Mp °C	$\alpha_D^{23.1^\circ C}$	Additional Data
<u>1</u>	1.0	179-80	—	Lit. mp. 181 ¹⁴
<u>4</u>	87	127-7.5	-160.9	" " 128 ¹⁵ ; Lit. $\alpha_D^{15^\circ C}$ -156.6 ¹⁵
<u>5</u>	36	150-1d	—	" " 150d ⁶
<u>6</u> ¹⁶	90	165-5.5	-80.0	" " 165-6 ⁶
<u>7</u> ¹⁶	92	174-4.5	-77.0	" " 174-5 ⁶
<u>8</u> ¹⁶	65	135-6	—	
<u>10</u> ¹⁶	90	122-3	-90.8	
<u>11</u> ¹⁶	47	140-1	-22.4	
<u>12</u> ¹⁶	80	133-4	-28.8	" " 133-4 ⁶
<u>13</u>	50.2	oil	+10.5	M/e 217.1067 (calc. for M ⁺ +H: 217.1078) ¹⁸
<u>14</u> ¹⁶	28.5	72-3	-5.1	
<u>15</u> ¹⁶	82	110-11	-46.8	M/e 200 (M ⁺ +H-OH); ¹³ Cnmr: 1CH ₃ , 3CH ₂ , 5CH, 1C=O
<u>17</u> ¹⁶	20	111-2	-12.8	M/e 212; ir 1778, 1752, 1738 cm ⁻¹
<u>18</u> ¹⁶	95	79-80	+8.1	M/e 212; ir 1783, 1752, 1738 cm ⁻¹

Selected ¹Hnmr data (δ /CDCl₃)¹⁷

- 4 H₁: 5.19, d, J_{1,9}=4; H₃: 6.19, dd, J_{3,4}=6, J_{3,5}=2; H₄: 4.94, dd, J_{4,3}=6, J_{4,5}=3; H₇: 5.88, dd, J_{7,6}=2, J_{7,10}=1; H_{10a,10b}: 4.76, s(br); OCOCH₃: 2.125, 2.119, 2.063, 2.055, 2.035.
- 7 H₁: 5.66, d, J_{1,9}=2.5; H₇: 5.91, dd, J_{7,6}=1.5, J_{7,10}=1.5; H_{10a,10b}: 4.707, 4.779, J_{a,b}=15.4; OCOCH₃: 2.126, 2.111, 2.065, 2.054, 2.000.
- 11 H₁: 5.62, s; OCOCH₃: 2.10, 2.07, 2.05, 2.03, 2.00.
- 12 H₁: 5.57, d, J_{1,9}=2; H_{10a,10b}: 4.12 d(br), J_{10,8}=6; OCOCH₃: 2.096, 2.070, 2.052, 2.037, 2.026, 2.004.
- 13 CHO: 9.67, d, J=3.
- 15 OH: 4.81 (DMSO-d₆), d, J=6 (D₂O labile); OH: 5.76 (DMSO-d₆), d, J=4 (D₂O labile); H₁: 5.09 (DMSO-d₆), d, J=4 (\rightarrow s/D₂O); COOCH₃: 3.59, s.

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 TI Hydrogenation of dehydrolinalyl acetate into linalool acetate on supported palladium catalysts
 AU Pak, A. M.; Sokol'skii, D. V.; Tsai, E. M.; Pogorel'skii, A. P.; Bakhtinov, A. A.
 CS Inst. Org. Katal. Elektrokhim., Alma-Ata, USSR
 SO Zh. Prikl. Khim. (Leningrad) (1980), 53(9), 2135-9
 CODEN: ZPKHAB; ISSN: 0044-4618
 DT Journal
 LA Russian
 AB The title process gave 98% linalool acetate using 2.3% Pd/BaSO4 treated with 7.6 times. 10-2 N Na2CO3 as the catalyst in 50% aq. Me2CHOH.
 IT 7440-05-3, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts contg., for hydrogenation of dehydrolinalyl acetate)
 RN 7440-05-3 HCAPLUS
 CN Palladium (8CI, 9CI) (CA INDEX NAME)

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Экспериментальные и расчетные значения D на различных ступенях каскада

№ опы- тов	Параметры				Режим процесса в опыте	Экспериментальные / расчетные значения на ступенях			
	K (мин ⁻¹)	τ (мин)	α	D^0		№ 1	№ 2	№ 3	№ 4
1	1.1	0.9	1.6	5.6	Экстракция	1.8/1.84	—/1.76	1.6/1.6	1.0/1.13
2	1.1	0.9	1.0	5.6	Реэкстракция	5.6/5.6	5.8/5.92	6.5/6.71	9.7/9.44
3	0.85	1.1	3.5	11.9	Экстракция	2.8/2.28	—/2.05	2.2/1.82	1.3/1.3
4	0.85	1.1	3.5	11.9	Реэкстракция	14.2/13	15.8/13.7	16.5/15	20/21

Интересно сопоставить режимы экстракционных операций, которые следуют из традиционного и предлагаемого методов расчета. В качестве примера рассмотрим процесс, осуществляемый методом противоточной экстракции одним растворителем. Примем, что для извлекаемого компонента $D^0=4$, $K=2$ мин⁻¹. Требуется определить τ , при котором на семи ступенях $\varphi < 0.01$.

Используя традиционные соотношения [1], несложно показать, что для выполнения указанных требований нет необходимости проводить процесс в условиях, близких к равновесным, т. е. при $\tau > 2.5$ мин, когда $D > 3.9$. Достаточно принять время контакта равным 0.8 мин, что соответствует $D=1.75$. Однако и эта величина τ не является предельной. Как показывают расчеты с использованием предлагаемых соотношений, минимальное значение τ составляет 0.56 мин. При этом значения D на 1—7 ступенях будут соответственно равны 1.89, 1.88, 1.86, 1.82, 1.74, 1.57 и 1.2, что обеспечит $\varphi < 0.01$. Умножение допустимого τ означает, что процесс можно проводить при соответственно больших расходах. Так, в рассмотренном примере допустимый расход фаз в 1.43 раза больше по сравнению с данными расчетов, проведенными без учета особенностей неравновесных процессов, и в 4.5 раза больше по сравнению с процессом, осуществляемым в равновесных условиях.

В ы в о д ы

Получены и экспериментально подтверждены соотношения для расчета экстракционных процессов, проводимых в неравновесных условиях. Эти соотношения могут быть рекомендованы для выбора наиболее экономичного режима экстракции.

Л и т е р а т у р а

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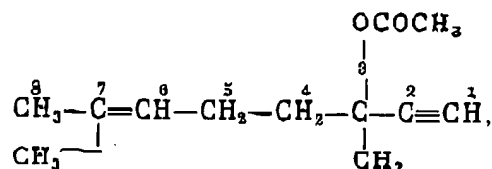
ГИДРИРОВАНИЕ ДЕГИДРОЛИНАЛИЛАЦЕТАТА В ЛИНАЛИЛАЦЕТАТ НА НАНЕСЕННЫХ ПАЛЛАДИЕВЫХ КАТАЛИЗАТОРАХ

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А. А. Базинков

В парфюмерной промышленности широкое применение находит ценное душистое вещество линалилацетат (ЛА). Обычно ЛА получают путем ацетилирования линалола уксусным ангидридом в присутствии фосфорной кислоты [1, 2] или путем пере-

этерификации гидрохлорида мирцена с ацетатом натрия [3]. Недостатком такого метода является низкий выход целевого продукта (60—68%).

Перспективным методом получения ЛА является селективное гидрирование ацетиленовой связи в сложной молекуле дегидролиналлацетата (ДеГЛА)



способной гидрироваться по нескольким направлениям. Обычно для этой цели используют катализатор Линдлара [4-6]. Выход ЛА составляет 93—94% [6].

Термодинамически наиболее вероятно гидрирование в первую очередь тройной связи в положении 1. В литературе практически отсутствуют данные о кинетике и механизме реакции гидрирования ДеГЛА.

ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

В работе гидрогенизация дегидролиналлацетата изучалась на обычной установке каталитического гидрирования по общепринятой методике в условиях, обеспечивающих протекание реакций в кинетической области [7]. В качестве катализаторов использовались нанесенные Pd-контакты, находящие широкое применение в процессах селективного гидрирования систем с тройной связью [4-6, 8, 9]. Величина удельной поверхности изученных катализаторов составляет для 2.3% Pd/BaSO₄ — 2.

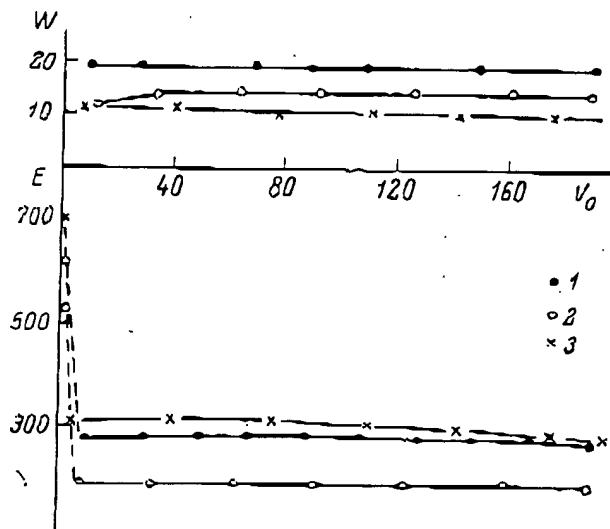


Рис. 1. Гидрирование дегидролиналлацетата в 50%-м изопропаноле при 30° и атмосферном давлении.

W — скорость гидрирования (мл/мин), V₀ — объем (мл), E — потенциал (мВ); то же для рис. 2. Катализатор (%): 1 — Pd/BaSO₄ (2.3), 2 — Pd/Al₂O₃ (2.3), 3 — Pd/CaCO₃ (5).

для 5% Pd/CaCO₃ — 6, для 2.3 Pd/Al₂O₃ — 53 м²/г. Навеска катализатора в единичном опыте составляет 0.02 г для Pd/Al₂O₃ и Pd/CaCO₃, 0.1 г — для Pd/BaSO₄.

Для гидрирования использовалось сырье, содержащее 88% ДеГЛА и 12% примесей. После гидрирования количество примесей не изменялось. Выход ЛА рассчитывался от содержания ДеГЛА. Гидрирование ДеГЛА проводилось в 50%-м изопропаноле при 30°. Процесс останавливали после поглощения одного моля водорода.

Вид кинетических кривых (рис. 1), специальные опыты с изменением концентрации ДеГЛА в исходном растворе и постоянство скорости гидрирования последовательно введенных порций вещества (рис. 2) указывают на нулевой порядок реакции по неопределенному соединению и высокую стабильность контактов.

Отношение адсорбционных коэффициентов $b_1/b_2 > 1$, т. е. исходный дегидролиналлацетат, характеризуется более высокой адсорбционной способностью, чем образовавшийся линаллацетат. Большое смещение потенциала при внесении навески

ДеГЛА ($\Delta E \sim 400-490$ мВ) говорит о том, что гидрирование сложного эфира протекает на обезводороженной поверхности катализатора.

По данным хроматографического анализа (табл. 1), во всех случаях насыщенный углеводород образуется к моменту поглощения моля водорода, при этом его содержание в катализате в зависимости от условий гидрирования меняется от 1 до 15%. В изопропаноле выход целевого продукта составляет 92% на Pd/BaSO_4 , 79 и 89% на $\text{Pd}/\text{Al}_2\text{O}_3$ и Pd/CaCO_3 соответственно.

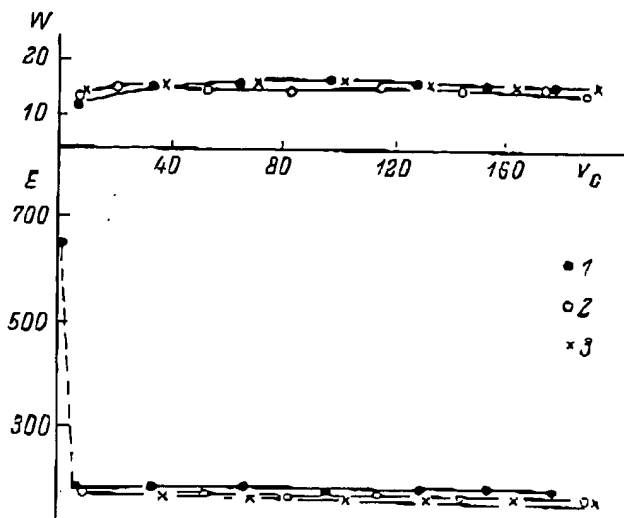


Рис. 2. Гидрирование последовательных порций дегидролиналилацетата в 50%-м изопропанол на 2.3% $\text{Pd}/\text{Al}_2\text{O}_3$ катализаторе.

Порция: 1 — I, 2 — II, 3 — III.

Наиболее низкий выход линалилацетата отмечается в воде и составляет 68%. Вероятно, после насыщения $\text{C}\equiv\text{C}$ -связи образовавшаяся $\text{C}=\text{C}$ -связь не снимается с поверхности, а гидрируется дальше до образования предельного углеводорода. При переходе к смешанному растворителю спирт-вода (1 : 1) выход целевого продукта возрастает и составляет для 2.3% $\text{Pd}/\text{Al}_2\text{O}_3$ — 92%, для 5% Pd/CaCO_3 — 91%. На Pd/BaSO_4 такого резкого увеличения выхода ЛА не наблюдается. Повышение давления водорода до 10 и затем 20 атм снижает выход ЛА на всех катализаторах (табл. 2); видимо, это связано с понижением энергии связи водорода с поверхностью константа с ростом давления [10].

Кинетические кривые гидрирования ДеГЛА на изученных катализаторах под давлением водорода приведены на рис. 3.

С целью повышения избирательности гидрирования ДеГЛА в ЛА проводилось в присутствии различных количеств сернистого кадмия (от $1 \cdot 10^{-4}$ до $1 \cdot 10^{-2}$ н.). Оказалось, что введение в каталитическую систему катионов кадмия по-разному влияет на выход целевого продукта в зависимости от катализатора, а именно: понижает до 81% на $\text{Pd}/\text{Al}_2\text{O}_3$, увеличивает до 96% на Pd/CaCO_3 или остается практически без изменения в случае Pd/BaSO_4 (табл. 1).

Известно [11-13], что специфически адсорбирующиеся катионы изменяют химический и структурный состав активных центров поверхности катализатора, энергию связи водорода с поверхностью, что отражается на избирательности процесса.

Добавка соды при гидрировании ДеГЛА на Pd/CaCO_3 не оказывает заметного влияния на выход ЛА. На остальных катализаторах в присутствии добавок соды в интервале от 0.03 до 0.1 г (т. е. от $2.3 \cdot 10^{-2}$ до $1.1 \cdot 10^{-1}$ н. Na_2CO_3) выход линалилацетата со-

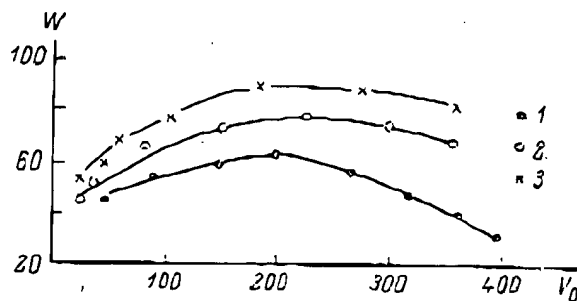


Рис. 3. Гидрирование дегидролиналилацетата в 50%-м изопропанол при 20 атм.

Обозначения те же, что для рис. 1.

ТАБЛИЦА 1

Гидрирование дегидролиналилцетата* на Pd-катализаторах при атмосферном давлении и 30°

Растворитель	Модифицирующие добавки	Состав катализатора (%)											
		2.3% Pd/Al ₂ O ₃				5% Pd/CaCO ₃				2.3% Pd/BaSO ₄			
		ДегЛА	ЛА	ДегЛА***	Выход ЛА от ДегЛА	ДегЛА	ЛА	ДегЛА	Выход ЛА от ДегЛА	ДегЛА	ЛА	ДегЛА	
Изопропанол	—	3.4	69.2	15.4	79	4.8	78.1	5.1	89	—	—	—	92
Вода	—	12.9	60.2	14.9	68	21.0	59.6	7.4	68	—	—	—	84
50%-й изопропанол	—	2.9	81.1	4.0	92	4.1	80.2	3.7	91	2.1	74.8	11.1	85
50%-й изопропанол	1·10 ⁻¹ в. CdSO ₄	7.4	74.7	5.9	85	1.0	84.9	3.1	96	3.5	76.3	8.2	87
	1·10 ⁻³ в. CdSO ₄	3.2	81.4	3.4	81	3.1	81.6	3.3	93	—	80.4	7.6	91
	1·10 ⁻² в. CdSO ₄	6.0	77.9	4.1	89	4.7	82.0	1.3	93	6.8	76.5	4.7	87
	2.3·10 ⁻² в. Na ₂ CO ₃	0.5	84.5	3.0	98	—	78.0	10.0	89	1.9	83.0	3.1	95
	7.6·10 ⁻² в. Na ₂ CO ₃	2.9	82.9	2.2	94	4.8	78.0	5.2	80	—	86.6	1.4	98
	1.1·10 ⁻¹ в. Na ₂ CO ₃	4.1	82.1	1.8	93	3.2	76.0	8.8	87	3.0	82.3	2.7	94

* К моменту гидрирования 1 моль водорода.

** Содержание примесей остается таким же, что и в исходном сырье.

*** ДегЛА — дегидролиналилцетат.

составляет 98% (табл. 1). Значение pH раствора при варьировании концентрации соды в указанном интервале изменяется от 6.5 до 11.7.

ТАБЛИЦА 2

Гидрирование дегидролиналилацетата на Pd-катализаторах под давлением водорода

P_{H_2} (атм)	Выход ЛА от ДегЛА (%)		
	Pd/Al ₂ O ₃	Pd/CaCO ₃	Pd/BaSO ₄
1	92	91	85
10	72	90	91
20	66	86	76

При введении щелочных добавок (например, Na⁺) происходит изменение строения двойного электрического слоя [16], приводящее к увеличению концентрации ионов Na на внешней обкладке. Вследствие этого наблюдается повышение энергии связи подорода с поверхностью катализатора и соответственно возрастание селективности процесса при гидрировании тройной связи.

Выводы

При изучении гидрирования дегидролиналилацетата в линалилацетат на нанесенных палладиевых катализаторах в различных растворителях показано, что подбор модифицирующей добавки позволяет повысить выход линалилацетата до 98%; это может найти применение в промышленности.

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L73 ANSWER 7 OF 9 HCAPLUS COPYRIGHT 2001 ACS
AN 1981:533174 HCAPLUS
DN 95:133174
TI Catalytic hydrogenation of dehydrolinalool and dehydrolinalyl acetate
AU Cerveny, Libor; Kuncova, Marcela; Ruzicka, Vlastimil
CS Dep. Org. Technol., Prague Inst. Chem. Technol., Prague, 166 28, Czech.
SO Collect. Czech. chem. Commun. (1981), 46(5), 1258-61
CODEN: CCCCAK; ISSN: 0366-547X
DT Journal
LA English
AB Hydrogenation of dehydrolinalool and dehydrolinalyl acetate in the liq. phase over Pd on CaCl₃ (partially deactivated by Pd) at 20.degree. under atm. pressure gave linalool and linalyl acetate with 99-99.5 and 95-6%, resp., selectivities.
IT 7440-05-3, uses and miscellaneous
RL: CAT (Catalyst use); USES (Uses)
(catalyst, for hydrogenation of dehydrolinalool and dehydrolinalyl acetate)
RN 7440-05-3 HCAPLUS
Palladium (8CI, 9CI) (CA INDEX NAME)

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CATALYTIC HYDROGENATION OF DEHYDROLINALOOL AND DEHYDROLINALYL ACETATE

Libor ČERVENÝ, Marcela KUNCOVÁ and Vlastimil RŮŽIČKA

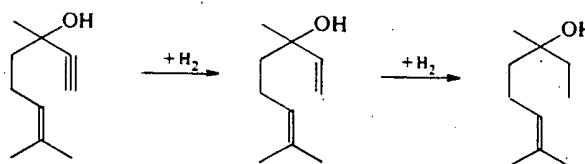
Department of Organic Technology,

Prague Institute of Chemical Technology, 166 28 Prague 6

Received June 25th, 1980

Catalytic hydrogenation of dehydrolinalool and of dehydrolinalyl acetate has been studied in the liquid phase under atmospheric pressure at 20°C with the aim to obtain selectively linalool and linalyl acetate. High selectivities have been obtained with the palladium on CaCO_3 catalyst which was partially poisoned by lead.

Linalool and linalyl acetate find use in perfume and pharmaceutical industry. They are synthesized by the selective catalytic hydrogenation of dehydrolinalool and dehydrolinalyl acetate which is most frequently carried out at ambient temperature under normal hydrogen pressure. For practical purposes the catalyst is nearly exclusively palladium, frequently modified in a number of ways¹⁻¹². Catalytic hydrogenation of dehydrolinalool can be described by Eq. (1). Hydrogenation of dehydrolinalyl acetate proceeds analogously. Linalool is the intermediate product in the above scheme of consecutive reactions. The final product, dihydrolinalool, is undesirable in most cases. The problem of catalytic hydrogenation of dehydrolinalool and dehydrolinalyl acetate involves the selective hydrogenation of the triple C—C bond to the double bond.



The present work deals with the study of solvent effects on the selectivity of hydrogenation of both compounds on two commercial palladium catalysts.

EXPERIMENTAL

Compounds used. Dehydrolinalool, dehydrolinalyl acetate, both freshly distilled (Astrid Prague — import), 96% ethanol, distilled (Spojené lihovary, Prague), octane, analytical purity grade (Jenapharm, Labor Chemie, Apolda, GDR), acetic acid, analytical purity grade (Lachema, Brno) catalysts: 0.5% Pd/ CaCO_3 -desactivated by lead (1.325 g Pb/g Pd) (Farmakon, Olomouc), 2.8% Pd/C (Chemické závody ČSSP, Záluží), particles ≤ 0.063 mm, electrolytic hydrogen (Technoplyn, Kyje).

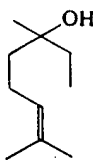
ROLINALOOL

ČOŽIČKA

Received June 23, 1981

linalyl acetate has been studied. The aim is to obtain selectively linalyl acetate with the palladium on CaCO_3 catalyst.

chemical industry. They are synthesized from linalool and dehydrolinalyl acetate which, under normal hydrogen pressure, are frequently modified in a number of ways. The reaction can be described by Eq. (1). Linalool is the intermediate product, dihydrolinalool, is under dehydrolinalool and dehydrolinalyl acetate. The C bond to the double bond.



effects on the selectivity of hydrogenation of linalyl acetate on palladium catalysts.

both freshly distilled (Astrich, Lachema, Brno), octane, analytical purity grade (Lachema, Brno), analytical purity grade (Lachema, Brno), 2 g Pd (Farmakon, Olomouc), 2 g electrolytic hydrogen (Technoprom, Olomouc).

Apparatus and procedure. All the measurements were carried out under atmospheric hydrogen pressure at 20°C in a standard apparatus¹³. In all runs, 10 ml of a solvent and 1 ml of the corresponding substrate were used. The weight amounts of the catalysts were changed within 0.027 to 0.80 g. The reaction course was followed by measuring time dependence of hydrogen consumption and by chromatographic analysis of the samples withdrawn from the reaction mixture at appropriate time intervals.

Analytical methods. Analyses were made on Chrom 4 instrument equipped with a flame ionisation detector, using glass columns (2.5 and 3.7 m long, 2.5 mm i.d.) packed with 15% Carbowax 20M on Chromaton NAW-DMCS, 0.16–0.20 mm particles, temperature 140°C.

RESULTS AND DISCUSSION

All the measurements were made under conditions which excluded the effect of mass transport on the course of hydrogenation¹⁴. The effect of external diffusion was avoided by efficient stirring, the eventual effect of internal diffusion was limited by using small granulation of the catalysts. Hydrogenation of dehydrolinalool and of dehydrolinalyl acetate was carried out in the presence of the following catalysts:

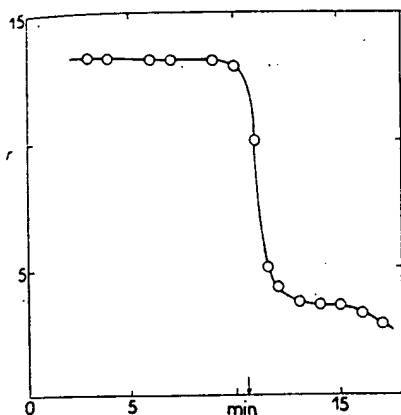


FIG. 1

Time Dependence of Rate of Hydrogenation, r (ml $\text{H}_2 \cdot \text{min}^{-1}$) of Dehydrolinalyl Acetate on $\text{Pd}/\text{CaCO}_3 + \text{Pb}$ Catalyst in Ethanol. Initial mixture: 1 ml of dehydrolinalyl acetate, 0.027 g of the catalyst and 10 ml of ethanol.

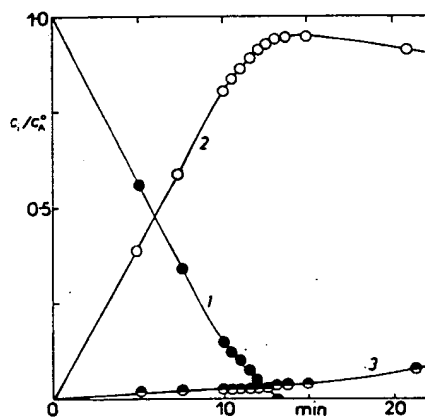


FIG. 2

Time Dependence of Concentrations of Substances in Hydrogenation of Dehydrolinalyl Acetate on $\text{Pd}/\text{CaCO}_3 + \text{Pb}$ Catalyst in Ethanol

c_i/c_A^0 the actual concentration of the component i related to the initial concentration of dehydrolinalyl acetate, 1 dehydrolinalyl acetate, 2 linalyl acetate, 3 dihydrolinalyl acetate.

0.5% Pd/CaCO₃ + Pb and 2.8% Pd/C and that always in ethanol, octane, and in acetic acid (the acid was not used in the case of the catalyst containing CaCO₃).

Typical experimental dependences are shown in Figs 1 and 2. From Fig. 1 it is obvious that the hydrogenation of dehydrolinalyl acetate proceeds at practically constant rate up to theoretical consumption of hydrogen necessary for hydrogenation of the triple to double C—C bond (designated by arrow). After disappearance of the triple bond, the reaction rate substantially slows down (several times) and the undesirable hydrogenation of the double bond of linalyl acetate proceeds to greater or smaller extent in all cases, producing dihydrolinalyl acetate. Time dependence of the concentrations of individual reaction components for the hydrogenation of dehydrolinalyl acetate is shown in Fig. 2. Analogous dependences were obtained also in all the other experiments.

From practical point of view, the most important factor is the selectivity of hydrogenation defined as the percentage amount of linalyl acetate (resp. linalool) in the

TABLE I
Selectivity of Hydrogenation of Dehydrolinalyl Acetate and Dehydrolinalool (%)

Solvent	Dehydrolinalyl acetate		Dehydrolinalool	
	0.5% Pd/CaCO ₃ -Pb	2.8% Pd/C	0.5% Pd/CaCO ₃ -Pb	2.8% Pd/C
Ethanol	95.0	83.0	99.0	80.0
Octane	96.0	86.0	99.5	nonspecific
Acetic acid		nonspecific		nonspecific

TABLE II
Initial Rate of Hydrogenation of Dehydrolinalyl Acetate and Dehydrolinalool
(ml H₂ min⁻¹ g_{cat}⁻¹)

Solvent	Dehydrolinalyl acetate		Dehydrolinalool	
	0.5% Pd/CaCO ₃ -Pb	2.8% Pd/C	0.5% Pd/CaCO ₃ -Pb	2.8% Pd/C
Ethanol	481	100	324	163
Octane	500	229	150	159
Acetic acid	—	67	—	114

always in ethanol, of the catalyst containing in Figs 1 and 2. From linalyl acetate proceeds at, hydrogen necessary for hydro (arrow). After disappearance down (several times) and linalyl acetate proceeds to linalyl acetate. Time components for the hydrologous dependences were

nt factor is the selectivity of linalyl acetate (resp. linalool)

nd Dehydrolinalool (%)

Dehydrolinalool	
0.5% Pd/CaCO ₃ -Pb	2.8%
99.0	
99.5	nonselective

nd Dehydrolinalool

Dehydrolinalool	
0.5% Pd/CaCO ₃ -Pb	2.8%
324	
150	
—	

chosllovak Chem. Commun. [Vol. 46]

ment of the disappearance of dehydrolinalyl acetate (resp. dehydrolinalool) from the reaction mixture. The difference from 100% represents the amount of dihydrolinalyl acetate and dihydrolinalool, respectively. The selectivities so calculated are presented in Table I. In those cases in which at 50% conversion of the starting compound the reaction mixture contained more than 10% of dihydrolinalyl acetate or dihydrolinalool were regarded as nonselective and were not followed up to the total conversion of the starting compound.

Of the two catalysts used, 0.5% Pd/CaCO₃ deactivated by lead turned out to be more suitable in all respects. Acetic acid was found to be unsuitable solvent. In non-polar octane, the selectivity of hydrogenation was higher than in polar methanol. In both cases the hydrogenation of dehydrolinalool was somewhat more selective than that of dehydrolinalyl acetate. With respect to the synthesis of linalyl acetate, the esterification of the already hydrogenated dehydrolinalool to linalool has not to be generally more advantageous compared to the esterification of dehydrolinalool followed by its hydrogenation, since one can expect that the esterification of the phenic substance will be accompanied by its polymerisation to the greater extent than in the case of the esterification of the substance of the acetylene-ethylenic type.

In Table II are presented the initial rates of hydrogenation of dehydrolinalyl acetate and of dehydrolinalool. Also from this aspect 0.5% Pd/CaCO₃ + Pb catalyst is more advantageous compared to the unmodified catalyst. The rate of hydrogenation of both substrates can be regarded as comparable, with the exception of the low rate of hydrogenation of dehydrolinalool in octane on Pd/CaCO₃ + Pb catalyst. The results obtained in this work are comparable with the most selective hydrogenations of the same substrates so far reported.

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TI Hydrogenation of allyl esters of saturated carboxylic acids in the presence of a nickel-titanium-aluminum catalyst
AU Il'khamdzhanov, P.; Mirkomilov, T. M.; Makhmudova, Z.
CS Tashk. Politekh. Inst., Tashkent, USSR
SO Uzb. Khim. Zh. (1991), (2), 45-7
CODEN: UZKZAC; ISSN: 0042-1707
DT Journal
LA Russian
AB Factors contributing to the optimization of hydrogenation of short-chain and fatty acid allyl esters in the presence of a Ni-Ti-Al catalyst were discussed. Among alc. solvents, the hydrogenation rate of caprylic acid was highest for MeOH and EtOH; the hydrogenation rate for fatty acid esters was max. in hexane and ligroine. The rate of hydrogenation increased with the rate of mixing in the range 100-400 shakes/min, and remained const. at higher shaking rates.
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П. ИЛЬХАМДЖАНОВ, Т. М. МИРКОМИЛОВ, А. Г. МАХСУМОВ, З. МАЛМУДОВА

ГИДРИРОВАНИЕ АЛЛИЛОВЫХ ЭФИРОВ НАСЫЩЕННЫХ КАРБОНОВЫХ КИСЛОТ В ПРИСУТСТВИИ Ni-Ti-Al- КАТАЛИЗАТОРА

Приведены результаты гидрирования аллиловых эфиров насыщенных карбоновых кислот C_2-C_{10} в присутствии промышленного Ni-Ti-Al-катализатора в среде односпиртовых спиртов, гексана и бензина на установке для каталитического гидрирования в жидкой фазе.

Гидрирование органических соединений, имеющих в структуре двойную связь, изучено достаточно хорошо. Есть сведения о гидрировании аллиловых эфиров кротоновой, фумаровой и олеиновой кислот на палладиевых и платиновых катализаторах [1]. Однако эти катализаторы из-за дороговизны в промышленности практически не применяются.

Необходимо расширять границы использования промышленных катализаторов для гидрогенизации органических соединений. В реакции гидрогенизации мы использовали промышленный скелетный Ni-Ti-Al-катализатор (47:3:50) и синтезированные ранее [2] аллиловые эфиры.

Поведение аллиловых эфиров $(CH_3-(CH_2)_n-CH=CH-O-CH_2-CH=CH_2)$

О
в реакции гидрирования

Самт. №	n	Навеска эфира (0,01 г-моль), г	Общий кол-во поглощенного H_2 , мл	Время полного гидрирования, мин	Йодное число эфира	
					до гидрирова- ния	после гидриро- вания
1	0	1,00	223	13	240	2,2
2	2	1,28	224	13	187	2,5
3	4	1,55	218	13	166	2,3
4	6	1,84	216	11	137	2,1
5	8	2,12	217	11	125	2,5
6	10	2,40	216	11	100	2,1
7	12	2,68	216	11	85	2,5
8	14	2,96	215	11	83	2,2
9	16	3,24	214	11	78	2,0

ры насыщенных карбоновых кислот жирного ряда (от уксусной до стеариновой). Процесс вели в жидкой фазе на установке для каталитического гидрирования [3]. Установлено, что аллиловые эфиры жирных кислот на исследуемом катализаторе, промотированном титаном, чрезвычайно легко гидрируются при атмосферном давлении и комнатной температуре. По данным о влиянии растворителя и интенсивности перемешивания на скорость реакции нашли оптимальные условия гидрирования.

Согласно [4], для проведения опытов в каталитическую «утку» загружали 1 мл Ni-Ti-Al-катализатора в 20 мл абсолютированного этанола. Всю систему продували 1—1,5 л водорода. Затем «утку» встряхивали при температуре опыта, катализатор насыщали водородом в течение 20—25 мин и затем через воронку в токе водорода добавляли навеску исследуемого эфира. Во избежание длительного контакта эфира с катализатором сразу же приводили в движение встряхивающий аппарат (300—350 односторонних качаний в минуту). Объем поглощаемого

мого водорода в начале гидрирования измеряли через каждую минуту, а затем, после стабилизации расхода его расхода, через каждые две минуты до полного прекращения поглощения.

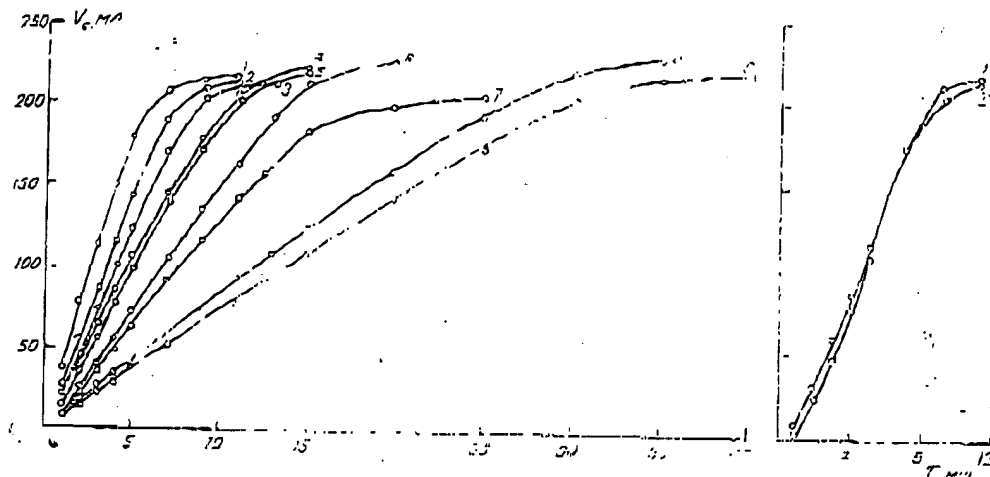


Рис. 1. Зависимость скорости поглощения водорода от природы растворителя (эфир — 2,12 г; интенсивность перемешивания — 300—350 односторонних качаний в минуту). 1 — метанол; 2 — этанол; 3 — пропанол; 4 — бутанол; 5 — пентанол; 6 — гексанол; 7 — гептанол; 8 — октанол; 9 — нонанол; 10 — деканол; 11 — гексан; 12 — бензин.

Установлено, что количество поглощенного водорода, необходимого для насыщения двойной связи, близко к теоретически рассчитанному (224 мл). Практически полное насыщение аллиловых эфиров карбо-

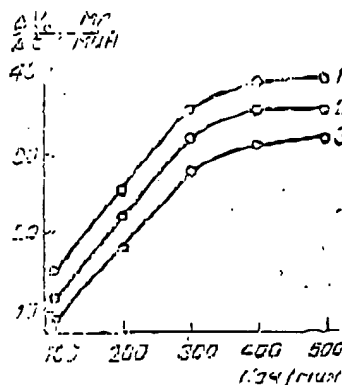


Рис. 2. Зависимость скорости гидрирования аллилкапроната от числа качаний «утки» при 20°C (1); 40 (2); 60 (3). (Условия аналогичны рис. 1).

новых кислот подтверждается и йодными числами гидрогенизатов (2—2,5% йода). Йодные числа исходных аллиловых эфиров жирных кислот, найденные экспериментально, постепенно уменьшаются от эфиров уксусной кислоты до стеариновой. Это объясняется, по-видимому, изменением кислотности карбонильной группы в зависимости от длины углеводородного радикала кислот. Получены данные о влиянии различных растворителей на скорость гидрирования аллиловых эфиров каприловой кислоты (рис. 1; опыт 4). Определено, что в ряду одноосновных алкогелей хорошими растворителями являются метиловый и этиловый спирты.

С увеличением углеводородного радикала спирта скорость гидрирования постепенно снижается, что связано, вероятно, с уменьшением растворяющей способности. Для изучения процесса гидрирования указанных эфиров в среде неполярного растворителя были проведены опыты в гексане и экстракционном бензине: оба также являются хорошими растворителями для гидрирования аллиловых эфиров жирных кислот (максимальная скорость процесса близка к скорости насыщения в среде метанола и этанола).

Проведены опыты по гидрированию аллилового эфира капроновой кислоты (№ 3) при различной температуре и интенсивности перемешивания в присутствии никель-титан-алюминиевого катализатора (рис. 2). Определено, что скорость насыщения аллилового эфира в этаноле при различных температурах растет в интервале 100—400 одно-сторонних качаний в минуту (начиная с 400 она остается почти постоянной). Аналогичные результаты получены на катализаторах $Ni-Fe-Al=47:3:50$ и $Ni-Cu-Al=45:5:50$ в интервале 300—350 качаний в минуту.

Повышение скорости гидрирования с увеличением числа качаний «утки» объясняется нарастающим контактом гидрируемых молекул эфира с активными центрами катализатора. Однако дальнейшая интенсификация перемешивания не увеличивает число контактов активных центров катализатора с ненасыщенными молекулами эфира, так как количество единовременных столкновений начиная с 400 качаний в минуту не изменяется.

Таким образом, установлено, что реакция гидрогенизации зависит от скорости перемешивания.

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РАДИКАЛЬНАЯ ПОЛИМЕРИЗАЦИЯ β -ХЛОРЕТИЛАКРИЛАТА В ПРИСУТСТВИИ ДОНОРНО-АКЦЕПТОРНЫХ ИНИЦИИРУЮЩИХ СИСТЕМ

Определены возможность низкотемпературной радикальной полимеризации β -хлорэтилакрилата в присутствии диметиланилина и кинетические параметры реакции. Вычислены энергии активации и порядок реакции по реагирующим компонентам. Предложена вероятная схема взаимодействия мономера с амином.

Данные о процессе полимеризации, протекающей с участием комплекса с переносом заряда, позволяют выявить механизм донорно-акцепторного взаимодействия при образовании первичных иницирующих радикалов полимеризации и осуществить регулируемую полимеризацию

Selective 1,4-Reduction of α,β -Unsaturated Carbonyl Compounds by Combined Use of Bis(1,3-diketonato)cobalt(II) Complex and Diisobutylaluminum Hydride

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Abstract: By the combined use of $\text{Co}(\text{acac})_2$ with DIBAL, various α,β -unsaturated carbonyl compounds such as enones, α,β -unsaturated carboxylates and carboxamides were selectively reduced in a 1,4-manner to obtain the corresponding 1,4-reduced products in good-to-high yields.

Key words: 1,4-reduction, diisobutylaluminum hydride, cobalt hydride, bis(acetylacetonato)cobalt(II) complex, α,β -unsaturated carbonyl compound

Metal hydrides are some of the most convenient and versatile reagents for the reduction of various organic compounds because they are easily handled.¹ Various metal-hydride reagents have been specifically developed for each type of reaction and a number of them are commercially available. For example, sodium borohydride (NaBH_4) and lithium aluminum hydride (LiAlH_4) are used for the reduction of carbonyl compounds into the corresponding alcohols in laboratories or industries, borane and its derivatives² were developed for the hydroboration of alkene, and diisobutylaluminum hydride (DIBAL) was applied for the selective reduction of esters or lactones into the corresponding aldehydes or lactols, respectively.³ Although a number of metal-hydride reducing agents have already been developed, few reports have discussed the chemoselective 1,4-reduction of α,β -unsaturated carbonyl compounds with metal-hydride reducing agents. It was proposed that the combined use of a copper salt⁴ with NaBH_4 or LiAlH_4 realized the 1,4-reduction⁵ of conjugate compounds and have been employed as a general method for the 1,4-reduction of α,β -unsaturated compounds. In the course of our study on the combinations of a cobalt complex and metal hydride, the reductive coupling reaction of α,β -unsaturated compounds with aldehydes using bis(1,3-diketonato)cobalt(II) complex with phenylsilane,⁶ and the enantioselective reduction of ketones or imines by the combined use of the optically active diiminato cobalt(II) complex with sodium borohydride⁷ were reported. In this communication, we would like to report that the combined use of the bis(1,3-diketonato)cobalt(II) complex with DIBAL was employed as a selective 1,4-reducing agent for α,β -unsaturated carbonyl compounds.

To a THF suspension of bis(acetylacetonato)cobalt(II) ($\text{Co}(\text{acac})_2$) was added an equimolar amount of a hexane solution of DIBAL at -78°C , then the red suspension immediately turned to a clear violet solution. This suggested

that cobalt-hydride was generated, and its reactivity was then compared with that of diisobutylaluminum hydride (DIBAL). It is well-known that DIBAL predominantly reduces α,β -unsaturated ketones to the corresponding allyl alcohols⁸ by a 1,2-reduction. Actually, 3-decen-2-one, (**1a**) was reduced to 3-decen-2-ol (**3a**) in 90% yield by 2.0 equivalents of DIBAL (Table 1, Entry 1). On the contrary, when **1a** was treated with the present reductant prepared from $\text{Co}(\text{acac})_2$ and DIBAL as mentioned above, the 1,4-reduced product, 2-decanone (**2a**) was selectively obtained in 96% yield (Entry 2). It is noted that chemoselection upon reduction with $\text{Co}(\text{acac})_2$ -DIBAL was completely different from DIBAL. A similar chemoselectivity distinction was observed for the reduction of α,β -unsaturated esters. Ethyl 2-octenoate (**1b**) was reduced to 2-octen-1-ol (**3b**) using DIBAL in 36% yield (Entry 3), whereas the 1,4-reduced product, ethyl octanoate (**2b**), was quantitatively obtained by treatment with $\text{Co}(\text{acac})_2$ -DIBAL (Entry 4). It was revealed that the combination⁹ of $\text{Co}(\text{acac})_2$ with DIBAL completely switched the chemoselectivity during the reduction of α,β -unsaturated carbonyl compounds to predominantly afford the 1,4-reduced product, whereas the 1,2-reduced product was formed with only DIBAL.

Table 1. Reduction of α,β -unsaturated compounds using DIBAL or $\text{Co}(\text{acac})_2$ -DIBAL^a

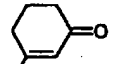
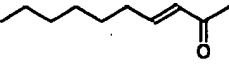
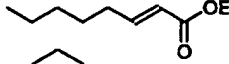
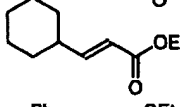
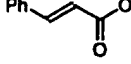
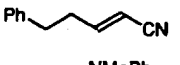
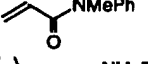
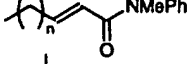
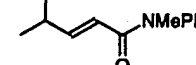
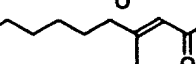
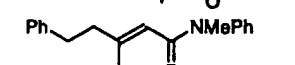
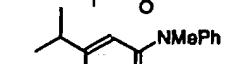
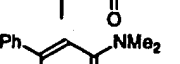
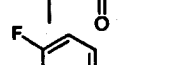
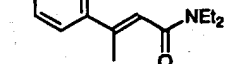
Entry	α,β -Unsaturated Compounds	Reductant	Yield/%	
			2	3
1		DIBAL ^b	0	90
2		$\text{Co}(\text{acac})_2$ -DIBAL	96	0
3		DIBAL ^c	0	36 ^d
4		$\text{Co}(\text{acac})_2$ -DIBAL	quant	0

^a Reductions were carried out using 0.5 mmol of substrate and 0.6 mmol of reductants under nitrogen atmosphere. ^b Two equivalents of DIBAL were used. ^c Two equivalents of DIBAL were used in hexane. ^d Starting material was recovered in 52% yield

The $\text{Co}(\text{acac})_2$ -DIBAL reductant was successfully applied to the reduction of a variety of α,β -unsaturated carbonyl compounds.¹⁰ As shown in Table 2, wide varieties of conjugated compounds were selectively 1,4-reduced in good-to-high yields. Cyclic enone, 3-methylcyclohexenone, was selectively converted to 3-methylcyclohexanone in

good yield by the 1,4-reduction as well as acyclic enones (Entries 1 and 2). α,β -Unsaturated esters having primary alkyl, secondary alkyl, and aryl group as substituents were cleanly reduced to their saturated ester in 70%-quant. yield (Entries 3-5). Also an α,β -unsaturated nitrile was converted to the saturated nitrile in good yield without any damage to the nitrile function (Entry 6). Amides of acrylic and alkenoic acids were reduced to the corresponding saturated amides in 82-90% yield (Entries 7-10). For the reduction of β,β -disubstituted amide, about two or three fold amounts of reducing agents were needed for complete conversion to afford their corresponding saturated amide in 82-99% yield (Entries 11-15).¹¹

Table 2. Reduction of α,β -unsaturated carbonyl compounds using

$\begin{array}{c} \text{R}^1 \\ \\ \text{R}^2 \end{array} \text{C}=\text{C} \begin{array}{c} \text{X} \\ \\ \text{O} \end{array} \xrightarrow[\text{THF, -78}^\circ\text{C to } 0^\circ\text{C}]{\text{Co(acac)}_2\text{-DIBAL}^a} \begin{array}{c} \text{R}^1 \\ \\ \text{R}^2 \end{array} \text{CH}_2\text{-CH} \begin{array}{c} \text{X} \\ \\ \text{O} \end{array}$			
Entry	Substrate	Procedure (Equiv.)	Yield/% ^b
1		A (2.0)	72
2		A (1.2)	96
3		A (1.2)	quant.
4		A (1.5)	96
5		A (1.5)	70
6		B (1.5)	60
7 ^c		B (1.2)	90
8		n = 4 B (1.2)	86
9		n = 7 B (1.2)	82
10		B (1.5)	88
11		B (2.0)	99
12		B (2.0)	82
13		B (3.0)	90
14		B (3.0)	92
15		B (3.0)	88

^a To a THF solution (7 ml) of Co(acac)_3 was added an equimolar amount of DIBAL in hexane, and subsequently a THF solution (3 ml) of substrate at -78°C . Procedure A: The mixture was gradually warmed to 0°C and stirred for 2 h. Procedure B: The reaction mixture was stirred for 4 h at 0°C . ^b Isolated yield. ^c 1.2 equiv. of Co(acac)_3 and 1.1 equiv. of DIBAL were used.

The present reaction could be explained as follows. During the Co(acac)_2 treatment with DIBAL, the color of the reaction mixture turned from dark red to dark violet. Based on these observations, it is reasonable to consider that a ligand-exchange reaction occurred between Co(acac)_2 and DIBAL to generate cobalt-hydride and (acetylacetonato)aluminum (Figure 1). The cobalt-hydride would then react with the α,β -unsaturated carbonyl compound in a 1,4-addition manner with weak chelation of the cobalt on the carbonyl oxygen. The resulting cobalt-enolate equivalent was collapsed by hydrolysis to afford the corresponding 1,4-reduced product.

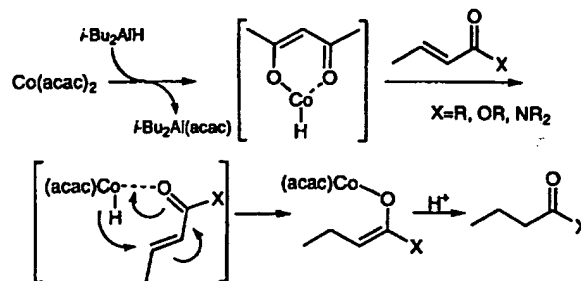


Figure 1

In summary, the combined use of Co(acac)_2 with DIBAL would immediately generate cobalt-hydride and it selectively reduced α,β -unsaturated carbonyl compounds in a 1,4-manner to obtain the corresponding 1,4-reduced product in good-to-high yields. It is expected that the present procedure would provide an alternative method for the 1,4-reduction of various α,β -unsaturated carbonyl compounds.

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- (10) Typical procedure: To a THF suspension (7 ml) of Co(acac)₃ (165.1 mg, 0.60 mmol) was added DIBAL in hexane (0.95 M, 0.63 ml, 0.60 mmol) at -78 °C, and the mixture was stirred for 10 min. A THF solution (3 ml) of ethyl 2-octenoate (85.2 mg, 0.50 mmol) was then added dropwise. The mixture was gradually warmed to 0 °C with stirring for a total of 4 h, and then the reaction was quenched by the addition of 1 M HCl (6 ml) solution. The products were extracted with ether and the combined extracts were washed with sat. NaHCO₃ and brine, then dried over anhydrous sodium sulfate. After evaporation of the solvents, the crude product was purified by silica gel column chromatography to give ethyl octanoate (85.8 mg, 99.5% yield).
- (11) Since the reactions proceed more slowly for congested substrates, part of the cobalt hydride species could be decomposed.

$$\frac{85.2 \text{ mg}}{3 \text{ ml}} =$$

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L73 ANSWER 6 OF 9 HCAPLUS COPYRIGHT 2001 ACS
 AN 1983:504731 HCAPLUS
 DN 99:104731
 TI Selective hydrogenation of unsaturated oxo compounds
 AU Sagindykova, S. M.; Kartonozhkina, O. I.; Konuspaev, S. R.
 CS USSR
 SO Deposited Doc. (1982), VINITI 3814-Pt.2-82, 66-9 Avail.: VINITI
 DT Report
 LA Russian
 AB The effects of inorg. salt additives on the hydrogenation of citral, 4-Me2CHC6H4CH:CMCHO (I), dehydrolinalool (II), and dehydrolinalool acetate (III) were examd. When citral and I were hydrogenated on Ni/Cr2O3, the selectivity for citronellal and 4-Me2CHC6H4CH2CHMeCHO was increased by several salts, esp. KI with citral and K2CO3 with I. In the hydrogenation of II on Pd/Al2O3, addn. of CdSO4 caused the reaction to stop after absorption of 1 mol H2; in the case of III absorption of 2 mol H2 occurred in the presence of CdSO4.
 IT 7440-02-0, uses and miscellaneous 7440-16-6, uses and miscellaneous

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имени П. ЛУМУМЫ

2.2.

МАТЕРИАЛЫ КОНФЕРЕНЦИИ МОЛОДЫХ УЧЕНЫХ

/МАТЕМАТИКА, ФИЗИКА, ХИМИЯ/

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№ 3814-82 ВХИ.

УДК 542.941:547.382

С.М.САГИНДЫКОВА, О.И.КАРТОНОЖКИНА, С.Р.КОНУСПАЕВ

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СЕЛЕКТИВНОЕ ГИДРИРОВАНИЕ НЕПРЕДЕЛЬНЫХ ОКСОСОЕДИ-
НЕНИЙ

Цитронеллаль (3,7-диметил октен-6-аль-I), цикламенальдегид (n-изопропил-α-метилгидрокориичный альдегид), линалоол и линалилацетат-ценные душистые вещества, применяющиеся в парфюмерной промышленности (I). Названные соединения получают избирательным гидрированием двойной связи, сопряженной с C=O связью, в α,β-ненасыщенных карбонильных соединениях: цитраля, форцикламена; тройной связи до двойной в молекулах третичного ацетиленового карбинола C-10 - дегидролиналоола (ДеГЛ) и его уксуснокислого эфира - дегидролиналилацетата (ДеГЛА).

Гидрирование проводилось на кинетической установке высокого давления (КУВД)/2/ при 2,02 МПа и при атмосферном давлении в "утке"/3/. Анализ проводился методом ГЭХ. Гидрирование цитраля, форцикламена изучено на $M-\text{Cr}_2\text{O}_3$ в 60% водном растворе изопропанола в присутствии добавок Na_2CO_3 , K_2CO_3 , KI , CdI_2 , ZnI_2 ; гидрирование ДеГЛ и ДеГЛА - CdSO_4 .

Параллельным изучением селективности гидрирования сопряженной этиленовой связи цитраля, форцикламена и физико-химических свойств $M-\text{Al}_2\text{O}_3$ /4/, $\text{Rh}/\text{Al}_2\text{O}_3$ /5/ установлено, что водород с теплотой адсорбции 71-63 кДж/моль и интервалом температур десорбции 343-593°K является ответственным за избирательное гидрирование двойной связи, сопряженной с карбонильной группой. Названные катализаторы проявляют высокую избирательность гидрирования этиленовой связи непре-

67

цельных альдегидов, что следует из таблицы I.

Табл. I. Гидрирование цитрала и форцикламена при 333°K и 0,101 МПа в этаноле

Выход дигидро-альдегидов, %	Катализатор	
	Ni-Al ₂ O ₃ (37% Ni)	Rh-Al ₂ O ₃ (5% Rh)
Цитронел-лаль	99,0	97,0
Цикламен-альдегид	77,0	91,0

Селективность процесса при гидрировании цитрала выше, чем в случае форцикламена. Последнее связано с особенностями электронного строения альдегидов.

Из квантовохимических расчетов/6,7/ следует, что при переходе от алифатических альдегидов к алкилароматическим α, β -непредельным альдегидам растет делокализация электронов. Порядок π -связи для изолированной двойной связи цитрала 0,998, сопряженной-0,869, карбонильной группы- 0,817, т.е. отмечается существенная разница в электронных плотностях этих связей. В молекуле форцикламена порядок π -связи в карбонильной группе 0,817, сопряженной двойной связи 0,823, т.е. в форцикламен-альдегиде порядок π -связи сопряженных этиленовой и карбонильной групп практически одинаков, что свидетельствует о полной делокализации электронов, обеспечивающей высокую активность карбонильной группы.

Табл. 2. Гидрирование цитрала, форцикламена на Ni-Cr₂O₃ при 393°K и 2,02 МПа в 60% изопропанол (после поглощения 1,0 моля H₂).

Добавка	Количество добавки, мг/г кат-ра	Содержание цитронеллала, %	Селективность	Содержание цикламен-альдегида, %	Селективность
-	-	81,0	89,0	82,0	89,1
Ni ₂ CO ₃	60	90,0	93,8	91,0	93,8
K ₂ CO ₃	180	72,0	78,3	/-	-
K ₂ CO ₃	120	68,0	72,3	92,0	94,8
K ₂ CO ₃	60	66,0	70,2	-	-
CdI ₂	38	94,0	96,9	75,0	86,2
CdI ₂	19	87,0	92,6	82,0	91,1
KJ	88,	93,0	96,9	79,0	88,8
KJ	44	97,0	98,0	-	-
ZnJ ₂	60	85,0	93,4	62,0	76,1

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При гидрировании цитраля на $Ni-Cr_2O_3$ максимальная селективность по цитронеллалу отмечается при внесении добавок KJ и составляет 98%. (табл.2). При гидрировании форцикламена наиболее высокая селективность по цикламенальдегиду на $Ni-Cr_2O_3$ получена при введении добавок K_2CO_3 , Na_2CO_3 и составляет 93-94%. На Ni -форматном, применяющемся в промышленности, выход цикламенальдегида составляет 50% /8/.

Микрокалориметрическое исследование $Ni-Cr_2O_3$ с добавками KJ и K_2CO_3 /9/ показало, что введение KJ резко снижает теплоту адсорбции водорода. Внесение добавок KJ и K_2CO_3 снижает величину металлической поверхности. Очевидно, внесение добавок K и K_2CO_3 изменяет энергетическую характеристику поверхности катализатора, адсорбированного водорода, и, соответственно, адсорбционные свойства поверхности по отношению к различным непредельным группам, с чем связано повышение селективности процесса.

Способы получения цитронеллала гидрированием цитраля на $Ni-Cr_2O_3$ с добавкой KJ и цикламенальдегида гидрированием форцикламена на $Ni-Cr_2O_3$ с добавкой K_2CO_3 внедрены на Колужском комбинате синтетических душистых веществ. Экономический эффект составляет 150 тыс. руб. в год.

При гидрировании ДеГЛ в спиртах C_2-C_5 - на 0,5% Pd/Al_2O_3 селективность составляет 99-100%, в случае ДеГЛА - 84-91%. При внесении добавок $CdSO_4$ гидрирование ДеГЛ самопроизвольно останавливается после поглощения моля водорода ($S=100\%$). В случае ДеГЛА реакция идет до поглощения 2-х молей водорода (рис). Различие в поведении ДеГЛ и ДеГЛА связано с особенностями их электронного строения /10/. В молекуле ДеГЛ у углерода, соседнего с тройной связью, расположена OH -группа, в случае ДеГЛА - эфирная группа $-OOCN_3$. При гидрировании ДеГЛ в линалоол гидроксильная группа увеличивает электронную плотность этиленовой связи, уменьшая этим её акцепторную способность /10/. Совершенно другой эффект оказывает сложно эфирная группа, которая проявляет сильную акцепторную способность, что увеличивает адсорбционную способность двойной связи линалилацетата и снижает селективность процесса.

69

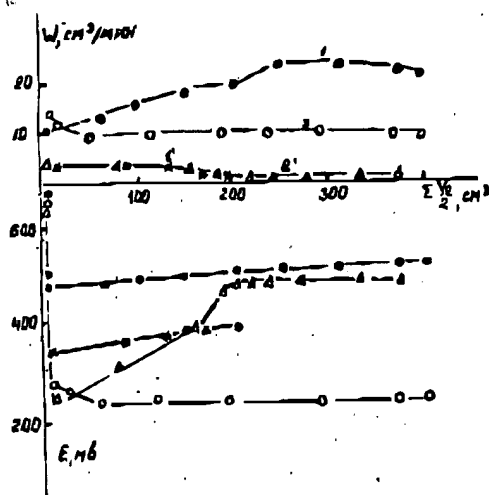


Рис. Гидрирование ДГЛ (1,1') и ДГЛА (2,2') на 0,5% $\text{Pd}/\text{Al}_2\text{O}_3$ при 303°K и 0,101 МПа. Кривые 1,2 — гидрирование без добавки; 1',2' — с добавкой CdSO_4

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BIODEGRADABLE POLYGLUTARALDEHYDE INJURY. K.I. Park^{1,2*},
Joll Med, Seoul, South Korea,
Materials Sci & Engineering,

fragment & foreign gene expression differentiation into neural cells in the injured brain, their parenchymal loss. To address this, we transplanted with NSCs into functional circuits. To test this, cells grew robustly & migrated. A NSCs/PGA unit was implanted into the injured brain & the unit & even becoming vascularized. Filament (NF)+ donor-derived NF+ fibers enter the brain in the cortical penumbra, many compared to those in the control complex facilitate even further growth/outgrowth of such cells to

327.10

SUCCESSFUL TRANSPLANTATION OF NEURONAL STEM CELLS IN THE GASTROINTESTINAL TRACT WITH EVIDENCE OF MORPHOLOGICAL AND FUNCTIONAL DIFFERENTIATION. M.A. Micci^{1*}, R.D. Learish², P.J. Pasricha¹. ¹Gastroenterology and Hepatology, UTMB at Galveston, Galveston, TX, USA, ²Promega Corporation, Madison, WI, USA. Several gastrointestinal motility disorders are characterized by a loss of critical neuronal subpopulations in the enteric nervous system. Replacement of the lost population of neurons is now potentially feasible using totipotent neural stem cells (NSCs). **Methods:** NSCs were obtained from the SVZ of Holtzman rats at embryonic day 17. Cells were co-cultured on a confluent layer of human intestinal smooth muscle (HISM) cells. NSCs were loaded with the NO-sensitive fluorescent indicator DAF-2 and relative fluorescence intensity (RFI) changes reflecting NO production were measured. In separate experiments, NSCs were labeled with CM-Dil and transplanted into the pylorus of wild-type mice. At 2, 4 and 8 weeks after transplantation, fluorescent double-labeling immunocytochemistry was performed on tissue sections using antibodies for β -tubulin and nNOS. **Results:** Our data shows that cultured rat NSCs differentiate into neurons and form anatomical contact with HISM cells *in vitro*. In addition we found that cultured NSCs express nNOS and produce NO. NO production was 6.90 RFI in the presence of L-arginine and significantly inhibited in the presence of L-NAME (1.92; $P < 0.001$). Following transplantation into the mouse gastrointestinal wall, Dil-labeled NSCs were found within or in close proximity to the myenteric plexus at all time points studied. Transplanted NSCs continued to express β -tubulin as well as nNOS. **Conclusions:** NSCs can form anatomical contact with smooth muscle cells, be successfully implanted into the gastrointestinal wall and express nNOS.

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DEMONSTRATE GLUTAMATE TRANSPORTER IN AN OTYPIC SPINAL CORD MODEL. T. Ho^{1*}, N.J. Maragakis¹, J. Lladó¹, C. Coccia¹, E.Y. Snyder², J.D. Rothstein¹. ¹Dept. of Neurology, Johns Hopkins Hosp, Baltimore, MD, USA, ²Dept. of Neurology and Pediatrics, Children's Hosp., Boston, MA, USA. Neural stem cells (NSCs) demonstrate the ability to differentiate into a variety of mature neuronal, astrocytic, and oligodendroglial phenotypes. Using organotypic spinal cord cultures, we have developed an *in vitro* model for studying stem cell biology. These cultures preserve local synaptic morphology as revealed by both light and ultrastructural studies with intact inhibitory and excitatory synapses between dorsal neurons, interneurons, and motor neurons. Furthermore, they can be maintained for up to three months *in vitro* with preserved biochemical and morphologic features. Using a murine NSC subclone C17.2 and human subclone H1, NSCs are transplanted onto the slices where they engraft and differentiate into neuronal phenotypes. These differentiated cells extend processes and interact with native motor neurons as well as other resident neurons. These cells, in their undifferentiated state, also exhibit tropic activity. NSCs on the cellulose membrane induce robust motor axon outgrowth toward the undifferentiated NSCs. These data suggest that these neural stem cells may be important not only for their ability to differentiate into resident spinal cord neurons but may also provide tropic support to native motor neurons. *Supported by: Project ALS.*

327.14

CELLS TRANSPLANTED IN A BLASTOMA MODEL. N.J. Maragakis¹, J. Lladó¹, C. Coccia¹, E.Y. Snyder², J.D. Rothstein¹. ¹Dept. of Neurology, Johns Hopkins Hosp, Baltimore, MD, USA, ²Dept. of Neurology and Pediatrics, Children's Hosp., Boston, MA, USA.

HUMAN EMBRYONIC ENDOTHELIAL CELLS: A NEW TOOL FOR THERAPEUTICAL APPROACH IN NEUROLOGICAL DISORDERS? M. Girelli¹, G. Alessandri², S. Pagano¹, L. Cova¹, F. Vitello¹, E. Grioni¹, M. Cavallaro¹, S. Etteri¹, E.A. Parati^{1*}. ¹Neuropharmacology, Neurological Institute "C. Besta", Milan, Italy, ²Microbiology, University of Brescia, Brescia, Italy

327.1

COMPARISON OF TRANSPLANTATION OF NEURAL STEM CELLS IN THE GASTROINTESTINAL TRACT WITH EVIDENCE OF MORPHOLOGICAL AND FUNCTIONAL DIFFERENTIATION. M.A. Micci^{1*}, R.D. Learish², P.J. Pasricha¹. ¹Gastroenterology and Hepatology, UTMB at Galveston, Galveston, TX, USA, ²Promega Corporation, Madison, WI, USA. Several gastrointestinal motility disorders are characterized by a loss of critical neuronal subpopulations in the enteric nervous system. Replacement of the lost population of neurons is now potentially feasible using totipotent neural stem cells (NSCs). **Methods:** NSCs were obtained from the SVZ of Holtzman rats at embryonic day 17. Cells were co-cultured on a confluent layer of human intestinal smooth muscle (HISM) cells. NSCs were loaded with the NO-sensitive fluorescent indicator DAF-2 and relative fluorescence intensity (RFI) changes reflecting NO production were measured. In separate experiments, NSCs were labeled with CM-Dil and transplanted into the pylorus of wild-type mice. At 2, 4 and 8 weeks after transplantation, fluorescent double-labeling immunocytochemistry was performed on tissue sections using antibodies for β -tubulin and nNOS. **Results:** Our data shows that cultured rat NSCs differentiate into neurons and form anatomical contact with HISM cells *in vitro*. In addition we found that cultured NSCs express nNOS and produce NO. NO production was 6.90 RFI in the presence of L-arginine and significantly inhibited in the presence of L-NAME (1.92; $P < 0.001$). Following transplantation into the mouse gastrointestinal wall, Dil-labeled NSCs were found within or in close proximity to the myenteric plexus at all time points studied. Transplanted NSCs continued to express β -tubulin as well as nNOS. **Conclusions:** NSCs can form anatomical contact with smooth muscle cells, be successfully implanted into the gastrointestinal wall and express nNOS.

327.

USE OF TRANSPLANTATION OF NEURAL STEM CELLS IN THE GASTROINTESTINAL TRACT WITH EVIDENCE OF MORPHOLOGICAL AND FUNCTIONAL DIFFERENTIATION. M.A. Micci^{1*}, R.D. Learish², P.J. Pasricha¹. ¹Gastroenterology and Hepatology, UTMB at Galveston, Galveston, TX, USA, ²Promega Corporation, Madison, WI, USA. Several gastrointestinal motility disorders are characterized by a loss of critical neuronal subpopulations in the enteric nervous system. Replacement of the lost population of neurons is now potentially feasible using totipotent neural stem cells (NSCs). **Methods:** NSCs were obtained from the SVZ of Holtzman rats at embryonic day 17. Cells were co-cultured on a confluent layer of human intestinal smooth muscle (HISM) cells. NSCs were loaded with the NO-sensitive fluorescent indicator DAF-2 and relative fluorescence intensity (RFI) changes reflecting NO production were measured. In separate experiments, NSCs were labeled with CM-Dil and transplanted into the pylorus of wild-type mice. At 2, 4 and 8 weeks after transplantation, fluorescent double-labeling immunocytochemistry was performed on tissue sections using antibodies for β -tubulin and nNOS. **Results:** Our data shows that cultured rat NSCs differentiate into neurons and form anatomical contact with HISM cells *in vitro*. In addition we found that cultured NSCs express nNOS and produce NO. NO production was 6.90 RFI in the presence of L-arginine and significantly inhibited in the presence of L-NAME (1.92; $P < 0.001$). Following transplantation into the mouse gastrointestinal wall, Dil-labeled NSCs were found within or in close proximity to the myenteric plexus at all time points studied. Transplanted NSCs continued to express β -tubulin as well as nNOS. **Conclusions:** NSCs can form anatomical contact with smooth muscle cells, be successfully implanted into the gastrointestinal wall and express nNOS.

327

FETAL TRANSPLANTATION OF NEURAL STEM CELLS IN THE GASTROINTESTINAL TRACT WITH EVIDENCE OF MORPHOLOGICAL AND FUNCTIONAL DIFFERENTIATION. M.A. Micci^{1*}, R.D. Learish², P.J. Pasricha¹. ¹Gastroenterology and Hepatology, UTMB at Galveston, Galveston, TX, USA, ²Promega Corporation, Madison, WI, USA.